



REMOVAL OF CRYSTAL VIOLET AND ACID GREEN DYE IN AQUEOUS SOLUTION USING BANANA PLANT-DERIVED SORBENTS

(Penyingkiran Pewarna Crystal Violet Dan Acid Green Dalam Larutan Akues Menggunakan Penjerap Berasaskan Pokok Pisang)

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Abstract

In this study, the sorption of crystal violet (CV) and acid green (AG) dyes from aqueous solution was performed using banana plant-derived sorbents. Kinetics for both dyes showed that percentage removal increased with a contact time until equilibrium, where it stays almost constant. For CV dye, the percentage removal was above 90% at equilibrium. On the other hand, the percentage removal of AG dye was between 44-54% for the three sorbents. To study the effect of sorbent dose, the dose of the sorbents used was varied from 1 to 100 g/L. From the results, it was observed that an increase in sorbent dose would result in an increase of percentage removal of both dyes. However, for CV dye, the percentage removal became constant after 10 g/L. The effect of pH was also determined for both dye removal, where it was found that CV dye was unaffected by pH change. However, the AG dye can be removed more in highly acidic conditions.

Keywords: acid green dye, crystal violet dye, banana plant-derived sorbents, sorption

Abstrak

Dalam kajian ini, penjerapan pewarna Crystal Violet (CV) dan Acid Green (AG) dari larutan akues dilakukan dengan menggunakan penjerap berasaskan pokok pisang. Eksperimen kinetik menunjukkan bahawa peratus penyingkiran meningkat dengan masa sehingga keseimbangan, di mana peratus ini akan kekal sama. Untuk pewarna CV, lebih 90% pewarna disingkirkan untuk ketiga-tiga penjerap yang digunakan. Peratus penyingkiran pewarna AG hanya antara 44-54% sahaja. Selain itu, eksperimen kesan dos penjerap untuk pewarna menggunakan dos penjerap dari 1 ke 100 g/L. Untuk kedua-dua pewarna, peningkatan dalam dos penjerap meningkatkan peratus penyingkiran. Namun begitu, untuk pewarna CV, dos yang lebih tinggi dari 10 g/L tidak meningkatkan peratus penyingkiran. Kesan pH terhadap penyingkiran pewarna menunjukkan yang pewarna CV tidak dipengaruhi oleh pH. Sebaliknya, pewarna AG hanya boleh disingkirkan dengan baik pada keadaan yang sangat berasid.

Kata kunci: pewarna acid green, pewarna crystal violet, penjerap berasaskan pokok pisang, penjerapan

Introduction

Banana residues are an abundant source from agricultural waste. Banana is cultivated for its fruits, and the rest of the plant becomes waste once the fruits are harvested. Several parts of banana commonly used for water treatment are banana pith [1, 2], banana stalk [3], banana frond [4], and pseudo stem [5]. The production of banana in

Malaysia had been consistent at an average of 300,000 tonnes per year for the last ten years [6]. Therefore, it is essential that the agriculture wastes produced from banana plantation to be disposed or reused to minimize the environmental impact.

Recently, application of cellulosic fibers as adsorbent has attracted scientists and researchers due to its massive usage as non-renewable sources and poor management of agricultural wastes which lead to environmental problems [7]. The natural cellulosic fibers are emerging as the novel low cost materials for environmental and industrial applications [8].

This study focuses on the use of three parts of banana plant fibers. They are the fibers from banana leaves, stem, and stalk that act as sorbents in removing the CV and AG dyes from water. Both dyes are triarylmethane dyes, with CV as cationic dye and AG as anionic dye. Dye is considered one of major pollutants in water [9]. The experiments were performed in batch mode. The adsorption kinetics, the effect of sorbent dose and the effect of pH were studied to determine the effectiveness of banana plant derived fibers as sorbents in removing the CV and AG dyes.

Materials and Methods

Materials

The dyes used were anhydrous CV dye (90.0%, Sigma, US) and AG dye (pure, Acros Organics). The sodium hydroxide (System, Malaysia) and nitric acid (69-70%, Merck, Germany) were prepared as 0.1M solution to adjust the pH of the dyes prior to experiment. The banana plants taken to prepare the sorbents were collected from Kota Samarahan, Sarawak area.

Preparation of sorbent

The banana sorbents used in this study were taken from three parts of the banana plant, which are the stem, stalk, and leaves. All three parts were cut into uneven shapes, about 2 cm in length. Then, the banana fibers were washed with deionized water several times before they were dried at room temperature for three days. The final drying was done in the oven at 60 °C for 24 hours. The dried sorbents were then grinded and sieved to particle size less than 500 µm. The prepared sorbents were kept in air tight containers prior to use.

Preparation of dye solution

The dye solutions of CV and AG were prepared similarly. A known quantity of dye was dissolved in 1000 mL of deionized water to prepare the desired concentration of 1000 ppm.

Batch sorption study

The kinetics of adsorption was studied at 25 °C, agitation speed of 200 rpm, initial pH 7, initial concentration of 1000 ppm, and sorbent dose of 10 g/L for CV dye and 60 g/L for AG dye. For the first ten minutes, the samples were taken every minute. After 10 minutes, the samples were taken every 5 minutes until the 30th minute. Afterwards, the samples were taken every 30 minutes until three hours. After the samples were taken, they were filtered and the residual solutions were analyzed using UV-Vis spectrophotometer (Thermo Scientific, model Evolution 201).

The effect of sorbent dose was studied at 25 °C, agitation speed of 200 rpm, initial pH 7, initial concentration of 1000 ppm, and contact time of 3 hours. The sorbent doses were varied 1 to 100 g/L. After three hours, the samples were filtered and the residual solutions were analyzed using UV-Vis spectrophotometer (Thermo Scientific, model Evolution 201).

The effect of pH was studied at 25°C, agitation speed of 200 rpm, initial concentration of 1000 ppm, sorbent dose of 10 g/L for CV dye and 60 g/L for AG dye, and contact time of 3 hours. The initial pH of solution were varied from 2 to 12. After three hours, the samples were filtered and the residual solutions were analyzed using UV-Vis spectrophotometer (Thermo Scientific, model Evolution 201).

Results and Discussion

Sorption kinetics

The study of kinetics is to determine the characteristics of sorption with respect to time. Figure 1 and Figure 2 show the percent removal of CV and AG dyes over time. The removal of both dyes exhibit similar trends. The percent removal increases sharply during the early part of sorption (in part I) of the graph. This is where the sorption occurs very fast because of the availability of sorption sites and sorbates. As the sorption sites are gradually filled and sorbates become less, the sorption of dye onto sorbents become slower, as shown in part II of the graph. In the last part of the graph, this indicates equilibrium of sorption, where there are no further sorption occurring due to saturation of sorption sites. For CV dye, the equilibrium time is faster than AG dye. The equilibrium time for CV dye is 60 minutes, whereas 120 minutes is needed to achieve equilibrium for AG dye. Previous works on sorption of CV dye demonstrated wide range of equilibrium time, from 120 minutes using modified spirulina [10] to 8 hours using modified rice husk [11]. For AG dye, there are little works done on sorption using natural fibers. Comparison of sorption time with other method such as photoelectrocatalytic process [12], showed similar equilibrium time with the ones used in this study.

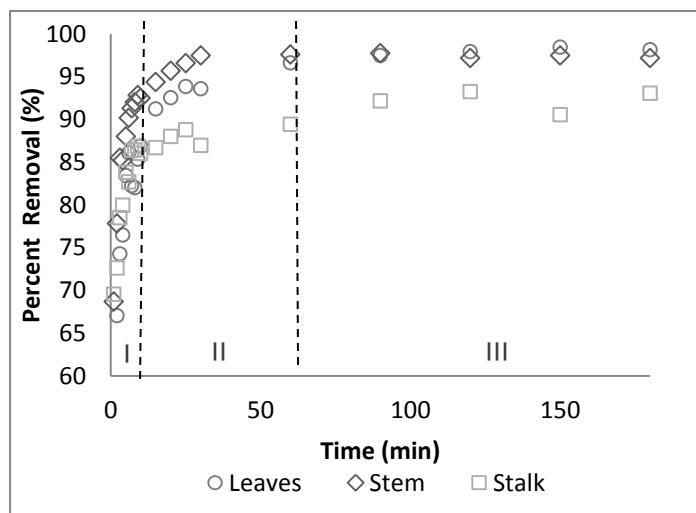


Figure 1. Percent removal of CV dye over time

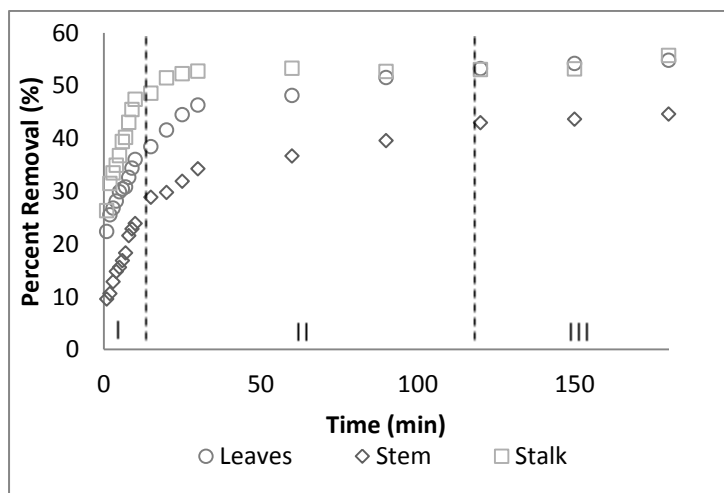


Figure 2. Percent removal of AG dye over time

The sorption of CV and AG dyes was fitted to 4 kinetics model, namely pseudo first order, pseudo second order, intraparticle diffusion, and Elovich, to determine the rate controlling step(s). The linear forms of these models were used to calculate the rate constants and coefficient of correlation. The linear forms for pseudo first order, pseudo second order, intraparticle diffusion, and Elovich are given as equations (1) to (4) below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

$$q_t = k_{id} t^{0.5} \quad (3)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where q_e is the equilibrium adsorption capacity in mg/g, q_t is the adsorption capacity(mg/g) at time t , k_1 is the rate constant for pseudo first order (min^{-1}), k_2 is the rate constant for pseudo second order (g/mg min), k_{id} is the rate constant for intraparticle diffusion ($\text{mg/g-min}^{0.5}$), t is time in minutes, α (mg/g-min) is the initial adsorption rate and β (g/mg) is the desorption constant.

The linearization fitting results are presented in Tables 1 and 2. For the CV dye removal, the sorption seems to fit very well with pseudo second order, with $R^2 > 0.999$, followed by Elovich>pseudo first order>intraparticle diffusion. The inclination towards pseudo second order indicates that the sorbate (CV dye) might be interacting with 2 sorption sites at one time. For the AG dye removal, however, all the kinetic models conform well to the sorption of the AG dye with $R^2 > 0.800$. Nevertheless, the pseudo second order model shows the best fit, followed by intraparticle diffusion > Elovich >pseudo first order. This indicates that there might be several rate controlling steps in the sorption of AG dye onto the banana fibers of the leaves, stem, and stalk which act as sorbents.

Table 1. Kinetics parameters for adsorption of CV dye onto banana leaves, stem, and stalk sorbents

	$q_{e, \text{exp}}$	$q_{e, \text{cal}}$	Pseudo first order		Pseudo second order		Intraparticle diffusion		Elovich		
			k_1	R^2	k_2	R^2	k_{id}	R^2	α	β	R^2
Banana leaves	93.7	21.0	0.09	0.8815	1.17×10^{-6}	0.9995	7.63	0.7075	1.536×10^3	0.095	0.8864
Banana stem	95.4	27.3	0.14	0.9453	6.73×10^{-7}	0.9999	4.86	0.7215	9.197×10^5	0.13	0.9045
Banana stalk	95.2	11.2	0.09	0.6567	3.93×10^{-7}	0.9997	3.79	0.6443	2.150×10^6	0.17	0.8442

Table 2. Kinetics parameters for adsorption of AG dye onto banana leaves, stem, and stalk sorbents

	$q_{e, \text{exp}}$	$q_{e, \text{cal}}$	Pseudo first order		Pseudo second order		Intraparticle diffusion		Elovich		
			k_1	R^2	k_2	R^2	k_{id}	R^2	α	β	R^2
Banana leaves	7.31	6.95	0.24	0.9356	4.08×10^{-4}	0.9962	1.80	0.9823	210.9	0.62	0.9832
Banana stem	12.1	5.28	0.27	0.8000	4.62×10^{-3}	0.9384	1.93	0.9542	8.201	0.60	0.8901
Banana stalk	14.3	8.32	0.26	0.9256	3.33×10^{-4}	0.9900	2.65	0.9848	75.78	0.43	0.9679

The effect of sorbent dose

The effect of sorbent dose is presented in Figure 3 (CV dye) and Figure 4 (AG dye). For CV dye, the increase in sorbent dose increases the percent removal of dye until saturation, where further increase in sorbent dose does not affect the percent removal. This is similar for all three sorbents, where the sorbent dose increase up to 10 g/L has positive effect on the percent removal of CV dye. As can be seen in Figure 3, the percent removal of CV dye using 10 g/L is already >90%, therefore further increase in sorbent dose results in constant percent removal.

The banana leaves, stem, and stalk sorbents does not remove a high percentage of AG dye, compared to CV dye. Increasing the sorbent dose up to 100 g/L only removes slightly more than 50 percent of AG dye. The sorbent dose cannot be increased further, as there will be little solution left for the analysis to proceed.

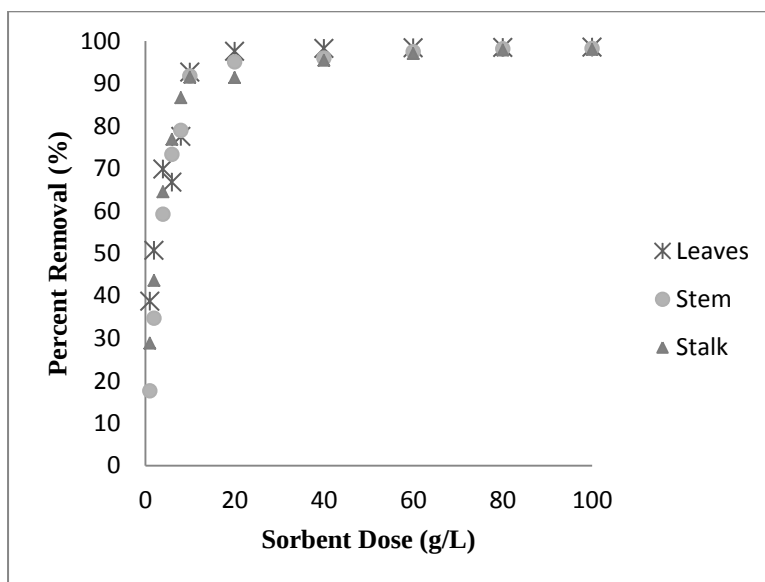


Figure 3. Percent removal of CV dye over sorbent dose

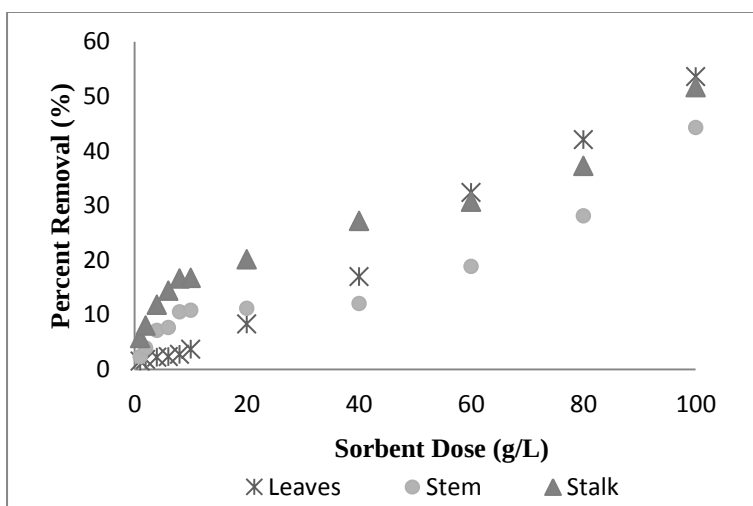


Figure 4. Percent removal of AG dye over sorbent dose

The effect of pH

The effects of solution pH on the CV and AG dye removal are presented in Figure 5 and Figure 7, respectively. The solution pH is an important factor in sorption process, as it affects the surface charge of an sorbent and therefore the interaction between the sorbent and sorbates is greatly affected. From Fig 5, it is shown that the initial solution pH does not affect the sorption of the CV dye onto the banana leaves, stem, and stalk sorbents. The percent removal remains almost constant with the increase of initial solution pH. The initial vs final pH from CV dye removal in Figure 6 shows that the final pH of 6 is attained when the initial pH is from 4-7. This finding is consistent with a study reported in literature. The CV dye adsorption using *Bacillus amyloliquefaciens* biofilm showed that at solution pH > 4, the solution pH did not affect the adsorption capacity [13]. In another study using modified rice husk, however, the increase in solution pH has a positive effect on adsorption, up until pH 10 [11]. The difference in solution pH effect towards adsorption capacity is due to the characteristic of the sorbents used. This is due to the difference of pH potential zero charge (pH_{pzc}) in each sorbent. A lower pH_{pzc} means that the surface charge of sorbent becomes negative at a lower pH, therefore can attract more adsorbate, which is cationic.

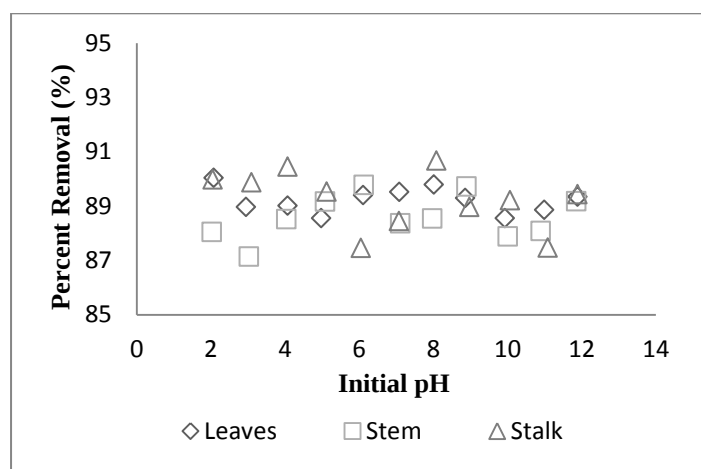


Figure 5. Percent removal of CV dye over initial pH

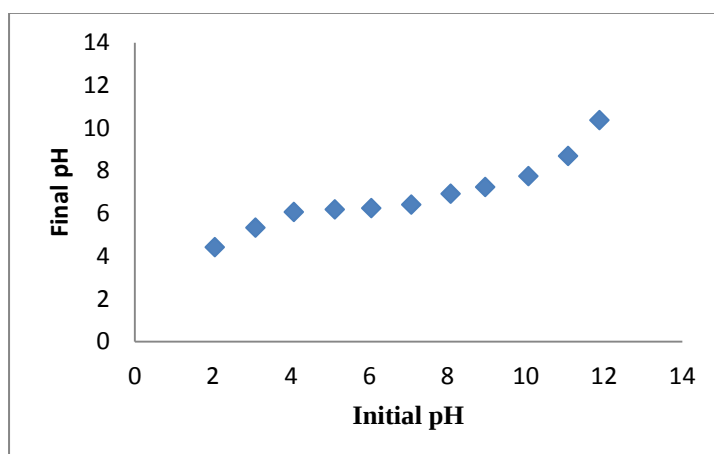


Figure 6. Initial vs final pH for CV dye removal

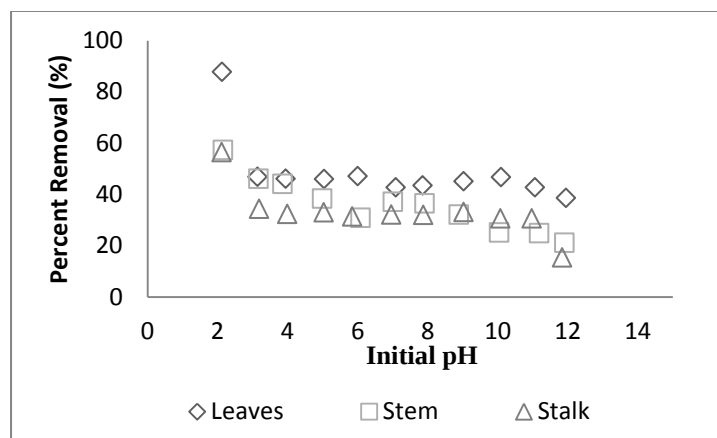


Figure 7. Percent removal of AG dye over initial pH

For the AG dye removal, only at high acidic condition (initial solution pH 2) the adsorption produces more than 50 percent removal. At higher the solution pH, the percent removal remains constant, and drops when starting from initial solution pH of 12. This finding is in line with the characteristic of the AG dye which is an anionic dye (negatively charged material). The AG dye compound will interact with the sorbent surface that is positively charged. For AG dye removal, most of its solution has a final pH 6 (for initial pH 3-8). At this buffer zone, the percent removal also remains constant. At final pH of 4, the percent removal is the highest, whereas the percent removal drops when the final pH is higher than 8.

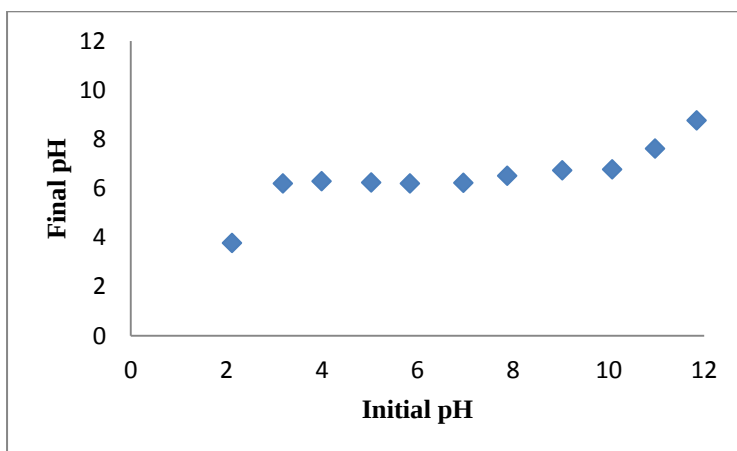


Figure 8. Initial vs final pH for AG dye removal

Conclusion

The removal of CV dye and AG dye can be performed using the banana leaves, stem and stalk sorbents. The percent removal of CV dye is more than 90% at equilibrium time of 60 minutes, whereas the AG dye can be removed up to 55% at equilibrium time of 120 minutes. The removal of both dyes fits closely to pseudo second order kinetics model. For CV dye, the increase of sorbent dose increases the percent removal of dye, until saturation. After 10 g/L sorbent dose, there is no further increase of percent removal. On the other hand, the percent removal of AG dye keeps increasing with increase in sorbent dose, up to 100 g/L. Further increase of sorbent dose is not possible due to limited solution available for analysis. The effect of pH is also determined for both dyes. For CV dye, the pH does not affect the percent removal whereas the AG dye can be removed better at initial pH of 2.

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