



ADSORPTION OF METHYLENE BLUE IN AQUEOUS SOLUTION BY MUSA PARADISIACA STEM POWDER

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ABSTRACT

In Malaysia, textile industry contributes the most to the wastewater that has led to environmental problems. Most of the dyes used in textile industries are toxic in nature with suspended carcinogenic and mutagenic effect that affects aquatic lives and human beings. The focus of this study is to identify the potential of Musa paradisiacal stem (banana stem) which commonly available waste material that are low-cost, natural and an eco-friendly bio-sorbent for the economical removal of methylene blue (MB) dye in aqueous solution. In this study, the stem is acting as an adsorbent. Batch model experiments are conducted to determine the effect of pH and the initial concentrations of MB solutions, adsorbent dosages and its contact time in methylene blue solutions towards the efficiencies and adsorptive (%) of the stem as a MB removal agent. The stem is dried and treated with Potassium Hydroxide to remove its lignin and to activate its cellulose part. The concentrations of MB solution are analyses using ultraviolet-visible spectrophotometry (UV-VIS) before and after the adsorption processes. The MB uptake has increased with the increased of pH value. The MB adsorption increased simultaneously with the adsorbent dosages and contact times. The maximum adsorptive is identified as 91.47% at 70 ppm of MB solution at pH 12 using 0.6 g of adsorbent dosage. The best adsorbent dosage is found to be as 0.6 g due to its higher adsorptive in all ranges of concentration and pH of the dye solutions. However, the removal percentage (%) decreases with the increased of initial MB concentrations. In conclusion, this study recommends that Musa paradisiacal can be used effectively in the adsorption of MB in aqueous solution.

Keywords: color removal, cationic dyes, mutagenic, water pollution, biosorption.

1. INTRODUCTION

Methylene Blue (MB) is a dye that forms a heterocyclic aromatic compound which consisting of dark green crystals. It is commonly used in textile and other industries such as rubber, food, paper, plastic, paint, cosmetic and pharmaceutical industry [1]. The dye has a highly toxicity that will give a bad effect on the aquatic lives [2]. It will reduce the oxygen content of water and this consequently avoids the photosynthesis of aqueous flora then impedes the solubility of gases in water [1]. Moreover, the human life will be infected with a serious disease due to the environmental instability caused by methylene blue that contained in the water [3]. Therefore, the removal of methylene blue from aqueous solution is important to prevent the continuous environmental pollution.

According to [4], many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. Hence, there are a lot of technique such as biological treatment, chemical oxidation, coagulation, ozonolysis, electrochemical degradation and reverse osmosis that have been investigated for removal of MB in aqueous solution [5]. Unfortunately, all listed methods are not widely used due to their high cost and economical disadvantage [6]. Amongst the numerous techniques, adsorption is the technique that is most widely used in the removal of dyes from aqueous solutions due to the low cost, sustainable, natural and eco-friendly biosorbent [7].

Adsorption is rapidly gaining prominence among the treatment technologies. In [7] noted that adsorption can

produce high-quality water, while also being a process that is economically feasible. The physical characteristics of the adsorbents such as surface area, porosity, size distribution, density and surface charge that have high influence in the adsorption process [8]. As a result, there has been a great interest in developing new adsorbent materials with diverse compositions, properties and functionalities

Normally, after harvesting the fruit, Musa paradisiacal stem is cut down and thrown away, mostly as a waste. This action has constantly caused the air pollution due to the open burning activity of the mass waste of Musa paradisiacal stem. Besides, it is also wasting the benefits that contain in the stem as it is actually possessed some valuable characteristic such as high in fiber. From the recent research, the stem contains about 60-65% of cellulose, about 6-19% of hemi-cellulose and 5-10% of lignin with 3-5% pectin [9].

Therefore, the purpose of this work is to investigate the ability of Musa Paradisiaca stem as an adsorbent of MB in aqueous solution. A batch model experiments are conducted to determine the effect of pHs and the initial concentrations of methylene blue solutions, adsorbent dosages and its contact time in methylene blue solutions towards the efficiencies and adsorptive (%) of the stem as a methylene blue removal agent.



2. MATERIALS AND METHOD

Preparation of adsorbent

The *Musa paradisiaca* stem was obtained from a nearby farmer at Kampung Bukit Besi, Dungun, Terengganu. The stem was cleaned and cut into a small shape. The stem was then dried under the sun for 2 days to remove its moisture content. After 2 days, it was dried in the oven at 55°C for 5 hours. Then, it was treated with Potassium Hydroxide (KOH) for a day to remove the lignin and to activate its cellulose content. After that, the treated stem was washed with distilled water. Again, the stem was dried for a day under the sunlight and continued drying in the oven at 55°C for 5 hours. To produce a stem powder, the dried stem was grinded using a dry blender and sieved using 250 micron size. Then the stem was weighted according to the dosage of 0.2 g, 0.4 g and 0.6 g [10].

Preparation of methylene blue solution

A stock of MB solution was prepared by dissolving 1 g of MB powder of 1000 ml distilled water in a volumetric flask. To prepare the desired concentration of MB solution, the formula of dilution was used. The 40 ppm and 70 ppm concentration of MB were prepared by dissolving separately a 40 ml and 70 ml of stock solution in 1000 ml of distilled water. The solutions were shaken vigorously for a few minutes to ensure complete dissolution [11].

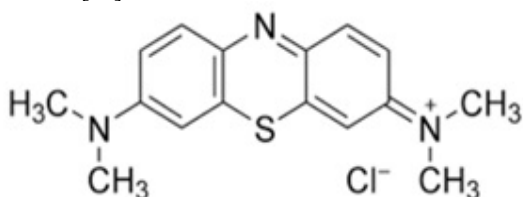


Figure-1. Chemical structure of methylene blue.

Preparation of different pH solution

The pH 2 of acidic solution was prepared by diluting 0.1 M hydrochloric acid (HCl) in the distilled water. Similarly, the alkaline solution with pH 12 was prepared by diluting 0.1 M sodium hydroxide (NaOH) in the distilled water. The pH meter was used to measure the pH.

Batch experiment

A batch model experiments were conducted to determine the effect of pHs and the initial concentrations of methylene blue solutions, adsorbent dosages and its contact time in methylene blue solutions towards the efficiencies and adsorptivity (%) of the stem as a methylene blue removal agent. For both 40 ppm and 70 ppm of MB solutions at pH 2 and pH 12, about 50 ml of the dye concentrations were poured into different 100 ml conical flask. The adsorbent dosage of 0.2 g, 0.4 g and 0.6 g were added into the flask. Then, the flasks were shaken

using an orbital shaker at 120 rpm for about one hour and 30 minutes [12].

Analysis study

The dye concentration was determined at every 15 minutes interval spectrophotometrically at the wavelength of 664.9 nm to the maximum absorbance by using ultraviolet-visible spectrophotometry (UV-VIS). [12]. The percentage removal of MB and amount of MB adsorbed on adsorbents (q_e) was calculated by Equation (1) and (2) respectively

$$\% \text{ removal} = 100(C_0 - C_e)/C_0 \quad (1)$$

$$q_e = C_0 - C_e / VM \quad (2)$$

Where q_e is the amount of dye adsorbed on adsorbent at equilibrium (mg/g), C_0 and C_e are the initial and equilibrium concentration (mg/L) of dye in solution, respectively, V is the volume of solution (L) and M is the mass of adsorbent (g).

3. RESULTS AND DISCUSSION

Effect of adsorbent dosage

The amount of dosage played an important role to determine the rate of adsorptive. As shown in Table-1, the maximum adsorption activity was happening using 0.6 g adsorbent in 70 ppm MB concentration at pH 12 as much as 91.47% within 90 minutes. However, the minimum adsorption activity of MB was recorded at 55.23% in 40 ppm MB concentration at pH 2 using 0.2 g adsorbent within 90 minutes. The results showed that the adsorption of MB was obviously influenced by the adsorbent dosage used during the adsorption process. The higher the dosages of the adsorbent the higher the percentage of adsorption [13]. This is due to the availability of the exchangeable sites or surface area of with larger amount of adsorbent was greater [14].

The amount of MB removal increased with increased surface area. It occurred when the surface area of the adsorbent was larger which provides a greater number of active sites for adsorption to happen [15]. This result was also supported by other researchers who reported that the higher adsorbent dosages contributed to the greater adsorption of MB. The larger the surface area and the availability of more adsorption sites was contributed from the larger amount of dosages [16].

Table-1. Effect of adsorbent dosage (g) on MB adsorptivity (%) within 90 minutes.

pH	Conc. (ppm)	Adsorbent Dosage (g)		
		0.2 g	0.4 g	0.6 g
		Final Adsorption Percentage (%)		
pH 2	40	55.23	65.38	81.20
	70	68.51	75.03	83.50
pH 12	40	87.99	89.68	90.41
	70	87.52	89.32	91.47



Effect of contact time

Contact time was evaluated as an important factor affecting adsorption efficiency. It was reported that the percentage of removal increased with increased contact time [17]. As shown in Figure-2-4, the trend of adsorptivity was increased with the increased contact time. The results show that at initial stages, the adsorption takes place rapidly on the external surface of the adsorbent. Then, it followed by slower internal diffusion process [18, 19]. This also due the surface sites at initial stages of contact time was larger to allow the adsorptivity.

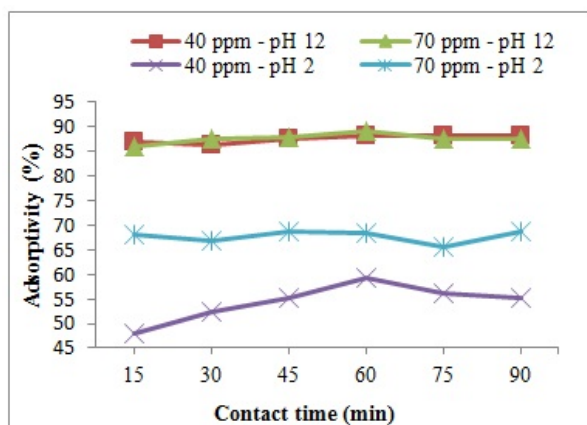


Figure-2. Effect on MB adsorptivity (%) with contact time (min) using 0.2 g adsorbent dosage.

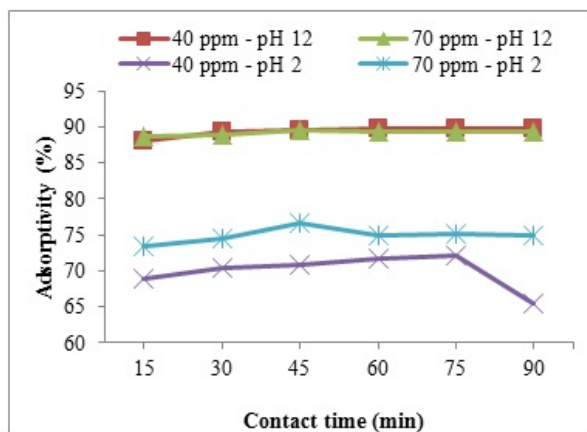


Figure-3. Effect on MB adsorptivity (%) with contact time (min) using 0.4 g adsorbent dosage.

As shown in Figure-3, during the usage of 0.4 g adsorbent dosage at pH 2 with a 40 ppm solution concentration, there was a significant decreased trend on MB removal which was from 72.18% to 65.38% at 75 to 90 minutes. It also happened at few adsorption processes as shown in these figures. It obviously showed a desorption occurred. The desorption happened after several lapse of time, which the surface of the adsorbent was harder to occupied and cause repulsion between the bulk phases and the solute

molecules of the solid. Thus, the time to reach an equilibrium was expected longer [18].

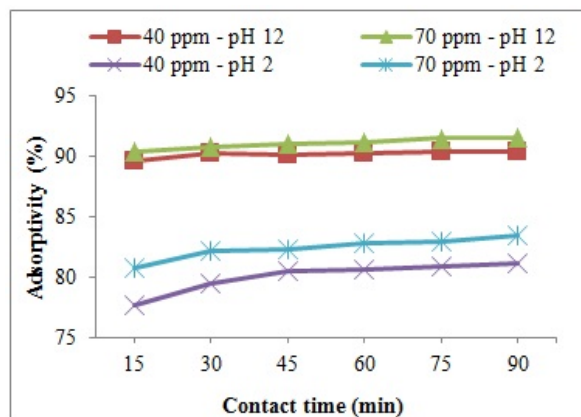


Figure-4. Effect on MB adsorptivity (%) with contact time (min) using 0.6 g adsorbent dosage.

Effect of initial dye concentration

The effect of initial concentration plays an important role to determine the percentage of adsorptivity. This was because adsorbent is sensitive over the concentration of the MB solution. The effect of initial MB concentration was carried out by preparing adsorbent of an adsorbate solution (40 ppm and 70 ppm). Overall, the higher the initial dye concentration of MB the higher the adsorptivity due to the concentrated of MB. Therefore, the higher the initial dye concentration, the surface of adsorbents that available to competing with ions in dyes was high hence the adsorption capacity was high [16]. It was because the interaction between the MB ions and the adsorbent molecules was higher and the mass transfer resistance between the aqueous and solid phase was lower [20]. Hence, the adsorption of MB becomes increase because the number of collisions between the dye molecules and the surface area of adsorbent was increased [21].

Effect of pH solution

One of the important factors affecting adsorption of metal ions is the pH of the solution. The effect of pH was studied between pH 2 and pH 12. MB is a cationic basic dye with molecular weight $C_{16}H_{18}N_3S \cdot 3H_2O$. As stated in Table-1, the maximum percentage of adsorption activity in 70 ppm MB at pH 2 and pH 12 were 83.50% and 91.47% respectively using 0.6 g adsorbent dosage. However, the minimum adsorption of MB in 40 ppm MB at pH 2 and pH 12 were 52.33% and 87.99% respectively using 0.2 g of adsorbent dosage.

Basically, the dissolved cationic dyes are positive charge in aqueous solution. At pH 2, the surface of the banana stem gathers the positive charge by adsorbing the H^+ ions that block the adsorption of methylene blue dye onto the adsorbent surface due to electrostatic repulsion [22]. This was because the MB cationic dye contains H^+ ion.



Besides that, for the alkaline, the number of negative charge OH^- in the alkaline solution increased due to electrostatic attraction between MB and pH alkaline [23].

Another researcher reported that when the pH value was higher than 10, the observation found that the removal of MB was decreased. This was happened due to solubilization of organic groups present on the surface of the absorbent. The initial pH affected the degree of ionization and the absorbent surface area. Ionization happened because of two different charge particles and resulting from and atom or molecules that lost its electron. The adsorption of dye was affected by the presence of hydrogen ion and hydroxyl ion in the solution. The changes of pH affected the absorption process through dissociation of functional groups in the absorbent surface area. This lead to a shift in reaction kinetics and equilibrium characteristic of adsorption process [24].

At lower pH, the hydrogen ion that was positively charged were attached to the surface area of absorbent. The surface charge became positive charge and electrostatic repulsion happened because of the MB was cations dye which was positively charged. It repulsed by each other, thus the adsorption of MB dye became lower. Therefore, the adsorption of MB at pH 12 was recorded higher mostly due to an electrostatic attraction. The solution was rich with hydroxyl ion that was negatively charged. It was attached to the surface area of absorbent and attracted the MB that have a positive charge. Thus, the maximum adsorption happened at pH 12 [25].

4. CONCLUSIONS

In the present investigation, it is clearly shown that Musa paradisiaca stem could be effectively used as a low cost adsorbent for the removal of MB from aqueous solution. The MB uptake increased simultaneously with pH, initial MB concentration and contact time. The removal of the MB increased when the adsorbent dosage increased from 0.2 to 0.6 g at different MB concentrations, 40 ppm and 70 ppm. The best adsorption activity condition, which resulted a maximum adsorptivity was using 0.6 g adsorbent in 70 ppm MB concentration at pH 12 that recorded as 91.47% of adsorptivity. As a whole, this study recommends that Musa paradisiaca stem can be used effectively in the adsorption of methylene blue in aqueous solution.

REFERENCES

- [1] Y. S. Al-Degs, M. I. El-Barghouthi, A. H. El-Sheikh and G. M. Walker. 2008. Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and Pigments*. 77(1): 16-23.
- [2] P. K. Malik. 2004. Dye removal from wastewater using activated carbon developed from sawdust: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*. 113(1): 81-88.
- [3] R. O. A. de Lima, A. P. Bazo, D. M. F. Salvadori, C. M. Rech, D. de Palma Oliveira and G. de Aragão Umbuzeiro. 2007. Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*. 626(1): 53-60.
- [4] K. Santhy and P. Selvapathy. 2006. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. *Bioresource Technology*. 97(11): 1329-1336.
- [5] Silva H. S., Martínez N. D., Deiana A. C. and González J. E. 2005. Catalytic oxidation of methylene blue in aqueous solutions. In: 2nd Mercosur Congress on Chemical Engineering. pp. 1-8.
- [6] G. Ciardelli, L. Corsi and M. Marcucci. 2001. Membrane separation for wastewater reuse in the textile industry. *Resources, Conservation and Recycling*. 31(2): 189-197.
- [7] K. K. Choy, G. McKay and J. F. Porter. 1999. Sorption of acid dyes from effluents using activated carbon. *Resources, Conservation and Recycling*. 27(1): 57-71.
- [8] A. O. Alade, O. S. Amuda, T. J. Afolabi and A. A. Okoya. 2012. Adsorption of naphthalene onto activated carbons derived from milk bush kernel shell and flamboyant pod. *Journal of Environmental Chemistry and Ecotoxicology*. 4(7): 124-132.
- [9] J. B. R. Marella, S. Madireddy and A. N. 2014. Maripi. Production of pulp from banana pseudo stem for grease proof paper. *International Journal of Engineering Research and General Science*. 2(1): 61-77.
- [10] T. Karthika, A. Thirunavukkarasu and S. Ramesh. 2010. Biosorption of copper from aqueous solutions using Tridax Procumbens. *Recent Research in Science and Technology*. 2(3): 86-91.
- [11] B. H. Hameed, A. M. Din and A. L. Ahmad. 2007. Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *Journal of Hazardous Materials*. 141(3): 819-825.
- [12] O. S. Amuda, A. O. Olayiwola, A. O. Alade, A. G. Farombi and S. A. Adebisi. 2014. Adsorption of methylene blue from aqueous solution using steam-activated carbon produced from lantana camara stem. *Journal of Environmental Protection*. 5(13): 1352-1363.



- [13] R. Jain and S. Sikarwar. 2008. Removal of hazardous dye congo red from waste material. *Journal of Hazardous Materials*. 152(3): 942-948.
- [14] A. Mittal, V. K. Gupta, A. Malviya and J. Mittal. 2008. Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials (Bottom Ash and De-Oiled Soya). *Journal of Hazardous Materials*. 151(2): 821-832.
- [15] S. A. Umoren, U. J. Etim and A. U. Israel. 2013. Adsorption of methylene blue from industrial effluent using poly (vinyl alcohol). *Journal of Materials and Environmental Science*. 4(1):75-86.
- [16] R. Gottipati and S. Mishra. 2010. Application of biowaste (waste generated in biodiesel plant) as an adsorbent for the removal of hazardous by-methylene blue-from aqueous phase. *Brazilian Journal of Chemical Engineering*. 27(2): 357-367.
- [17] R. Zeynolabedin, P. Moradihamedani, A. Bazyar and A. Marjani. 2015. Removal of methylene blue dye from aqueous solutions by *elaegnus gastifolia* as an adsorbent. *Oriental Journal of Chemistry*. 31(1): 271-276.
- [18] S. J. Allen and B. Koumanova. 2005. Decolourisation of water/wastewater using adsorption. *Journal of the University of Chemical Technology and Metallurgy*. 40(3): 175-192.
- [19] D. Gialamoudis, M. Mitrakas and M. Liakopoulou-Kyriakides. 2010. Equilibrium, thermodynamic and kinetic studies on biosorption of Mn (II) from aqueous solution by *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells. *Journal of Hazardous Materials*. 182(1): 672-680.
- [20] H. I. Maarof, B. H. Hameed and A. L. Ahmad. 2003. Adsorption equilibrium of phenols from aqueous solution using modified clay. *Jurnal Jurutera Kimia Malaysia*. 3: 85-94.
- [21] H. Masrosemal, H. Mas and S. Kathiresan. 2009. The removal of methyl red from aqueous solutions using banana pseudostem fibers. *American Journal of Applied Sciences*. 6(9): 1690-1700.
- [22] P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi and S. Sivanesan. 2010. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*. 261(1): 52-60.
- [23] N. K. Amin. 2009. Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*. 165(1): 52-62.
- [24] K. G. Bhattacharyya and A. Sharma. 2005. Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder. *Dyes and Pigments*. 65(1): 51-59.
- [25] B. H. Hameed and M. I. El-Khaiary. 2008. Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull. *Journal of Hazardous Materials*. 155(3): 601-609.