Colour Removal of Methylene Blue by Using Prepared Heat and Acid Treated from Toddy Palm Leaves as Biosorbents

Yu Yu Htun[1], Cho Cho[2], Zaw Naing[3]

ABSTRACT

In the present research, the plant-base waste material toddy palm leaf was prepared to be used as adsorbent for the removal of methylene blue from aqueous solution. The heat treated and acid treated toddy palm leaf powder (HTTPLP, ATTPLP) were used as an adsorbent in this research. The physicochemical properties of collected toddy palm leaf sample (TPLP, HTTPLP, ATTPLP) such as pH (8.5, 8.1, 7.9), moisture content (7.6%, 5.4%, 5.1%), bulk density (0.21, 0.19, 0.22), ash content (15.7%, 7.8%, 8.9%) and surface area (241.40, 288.18, 386.68) were observed respectively. The toddy palm leaf powder were characterized by modern techniques such as SEM. Surface morphology of toddy palm leaf samples were observed samples that channels with pores, more voids and porous character and sponge like with rough surface particles. The adsorption capacity of prepared samples were determined at different parameters such as, initial concentration, dosage of adsorbent and contact time. The dye removal of toddy palm leaf samples were studied by using model dyes (methylene blue). The maximum percent removal of dye has been achieved by using initial concentration of 60 mgL^{-1}, 0.06 g of dosage, 150 rpm and 1 h contact time. The removal percent of methylene blue (MB) by heat treated and acid treated toddy palm leaf powder were found to be (82.11%) and (97.52%), respectively. It was indicated that the toddy palm leaf samples were cheap and low cost effective biosorbent for the color removal of methylene blue from aqueous solution.

Keywords: Toddy palm leaf, Biosorbents, SEM, Methylene Blue

Introduction

Toddy Palm Leaf

The toddy palm tree (*Borassus flabellifer*) is a member of the family *Arecaceae* (palm family) and the only species of the genus *Borassus flabellifer*. The toddy palm is a robust tree and can reach a height 30 meters (98 ft.) toddy palm plant and toddy palm leaf were shown in figure (1). The trunk is grey, robust and ringed with leaf scars, old leaves remain attached to the trunk for several years before falling cleanly. The leaves are fan-shaped and 3 m (9.8 ft.) long, with robust black teeth on the petiole margins. After pollination, these blooms develop into fleshy fruits 15-25 cm wide, each containing 1-3 seeds. The fruits are black to brown with sweet, fibrous pulp and each seed is enclosed within a woody endocarp. They form a regular part of the diets of many people in the tropics and subtropics. (Bayton, Ross P. 2007).

Biosorption

Biosorption is a physiochemical procedure that takes place in a certain biomass which allows it to accumulate and attaches contaminants onto its cellular structure (Volesky, 1990). Though the use of biomass for environment purposes has been in practice for long, researchers are hopeful that the method will lead to an alternative economical method for the removal of color and heavy toxic substances from wastewater.

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Figure (1) Toddy Palm Plant and Toddy Palm Leaf.

Physisorption and Chemisorption

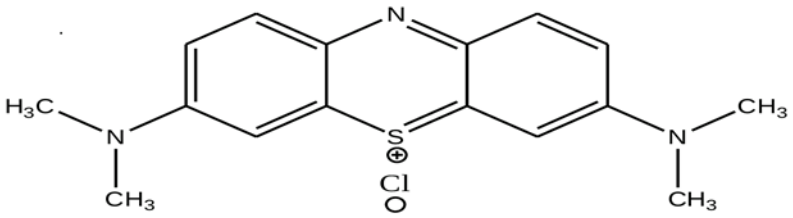
This is the type of adsorption in which the adsorbate adheres to the surface only through van der Waals (weak intermolecular) interactions. The forces are responsible for the non-ideal behaviour of real gas.

This is the type of adsorption where by a molecule adheres to a surface through the formation of a chemical bond. The forces are opposed to the van der Waals force (Malik, 2003).

Sorption Isothermal Modeling

Sorption isothermal modeling is fundamental to the industrial application of biosorption because it provides information for comparing different biosorbent under various operational conditions, design, and optimization procedures (Bengulella and Benaissa, 2002). In the present study, two parameter models were examined, namely, the Langmuir and Freundlich isotherms, to fit the data.

Methylene Blue



Methylene blue (3, 7 bis Dimethylamino-phenazathionium chloride)

Molecular formula - $C_{16}H_{18}N_3SCL$

Molecular mass - 319.85gmol^{-1}

Methylene blue, also known as methylthioniumchloride, is a medication and dye. Methylene blue is highly stable in the human body, and if ingested, it resists the acidic environment of the stomach as well as the many hydrolytic enzymes present. It is not significantly metabolized by the liver, and is instead quickly filtered out by the kidneys. Therefore, it is necessary to make sure the effluent contained methylene blue was treated first before released it to environment (Sharifah, 2006).

Removal of Organic Dyes by Adsorption Process

Dyes are widely used in textile, paper, plastic, food and cosmetic industries. The wastes coming from these industries can effect on our atmosphere causing pollution. The level of the pollutants even in very low concentration is highly visible and will affect aquatic life as well as food web. The number of conventional methods are available for colour removal from industrial effluents including ion exchange, adsorption, membrane technology and coagulation (Tahir *et al*., 2008).

Effectiveness of physico-chemical methods varies and depends on the type of dyes being eliminated. Each dye is, in most cases, a complex organic compound. It is an electronegective nature depending on pH of the solution. Total elimination of dyes can be achieved by application of coagulation together with sorption. The coagulation should be performed through addition of two reagents in a specifically determined proportioning sequence. The dyes from the solution are precipitated together with a sediment which is a product of a reaction between the reagents (coagulants) supplied to the solution (Anielak, 1996).

The presence of synthetic dyes in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1ppm. Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration. Due to low biodegradablity of dyes a conventional biological treatment process is not very effective in treating a dye wastewater. Adsorption of the molecules onto various adsorbents is an ideal option for decolourization, which is evidenced by the effectiveness of adsorption for various types of dye (Benaissa, 2005).

Many dyes are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion. Contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non-biodegradable characteristics. So, it is great interest to assess the ability of locally available toddy palm leaf plant for color removal of dyes from aqueous solution.

Materials and Methods

Toddy Palm Leaf was collected from Hinthada Township, Ayeyawady Region. The collected samples were cut into small pieces. The samples were washed thoroughly with tap water, sun dried at ambient temperature and ground into fine powder as shown in figure (2).

Figure (2) Toddy palm leaf samples and powders

Dried toddy palm leaf powder was sieved into size of 100μm. The powder was then soaked and washed severally with cold tap water until clean. Clean toddy palm leaf powder were soaked for 2 hours in hot water, and then the samples were filtered and rinsed with distilled water to obtain pH 7. Then dried again in oven at 80°C for 24 hours. Samples of dried toddy palm leaf powder (20 g) were carbonized at different times in and electric furnace. The carbonization process carried out in a furnace with respect to time of 1 hour at fixed temperature of 200°C, 250°C and 300°C. The heat treated toddy palm leaf powder was obtained. About 56 g of 100 mesh prepared toddy palm leaf sample was placed in a 250 mL conical flask. 336 mL hydrochloric acid (HCL) (2% v/v) was added into toddy palm leaf powder in a conical flask and then placed at room temperature about 24 hours. This mixture was filtered and washed by distilled water until the neutral pH. And then filtered by using filter paper and dried before using for adsorption purpose in electric oven at 105 °C (Nabilah *et al*., 2011).

The dye solution, Methylene Blue (MB) was studied. Analyses were carried out by colorimetric method using 2550, U.S.A Spectrophotometer and calibration curve of dye stuff solution were plotted. Based on the calibration curve or by using absorption coefficient (ε), concentration of dye solution was calculated.

Using the equilibrium contact time the nature sorption properties of various dyes was evaluated. Exactly 25 mL of dye solution of known initial concentration was mixed with a required dose of toddy palm leaf powder samples in the flask. The flask was placed on a magnetic stirrer at room temperature and was stirred for 1 hour. After one hour the samples were filtered and measured the absorbance. The percentage of color removal of heat and acid treated toddy palm leaf powder were also calculated (Ming, 2011).

A stock solution of 100 mg L^{-1} was prepared by dissolving 0.1 g of dye powder in 1000 mL distilled water. Dye solutions of different concentrations were then prepared by dilution on the stock solution with distilled water.

The prepared samples of toddy palm leaf powder were used to determine the physicochemical properties such as moisture content, pH, bulk density, ash content and surface area. These samples were characterized by using SEM analysis.

Results and Discussion

The physicochemical properties of toddy palm leaf powder (TPLP), heat treated (HTTPLP) and acid treated toddy palm leaf powder (ATTPLP) have been studied. The moisture content of (TPLP, HTTPLP, ATTPLP) were observed 7.6% 5.1% and 5.4% respectively. The pH value 8.5 (TPLP), 8.1 (HTTPLP) and 7.9 (ATTPLP) were observed. In general, the ash content in attributed to sow non-volatile minerals. So the ash contents of (TPLP, HTTPLP, ATTPLP) were found to be 15.7%, 7.8% and 8.1% respectively. The bulk density had 0.21gcm^{-3} (TPLP), 0.19 gcm^{-3} (HTTPLP) and 0.22 gcm^{-3} (ATTPLP). The material is apparently porous and has a higher surface area of particle. The surface area of (TPLP, HTTPLP, ATTPLP) were found to be 241.40 m^2g^{-1}, 288.18 m^2g^{-1} and 386.68 m^2g^{-1} respectively.

Figure (3) shows the effect of initial concentration of dyes (MB) onto the toddy palm leaf powder samples. The initial concentrations were varied from 20 mgL^{-1} to 100 mg L^{-1}. According to the experimental data, the removal percent decreases with increasing the initial concentration. It was observed that the removal percent of heat treated was greater than that of acid treated.

Efficiency (0.02 to 0.1) increases with the little decrease of adsorbent dose in methylene blue. The lower percent removal may be attributed to the normal quantity of sorbent dose is being used. This is due to increase in adsorbent dose attributed to increase in surface area and availability of adsorption site. From that data, acid treated was more effective than that of heat treated by using toddy palm leaf powder. The optimum sorbent dosage was found to be 0.06 g for methylene blue such shown in figure (4). The percentage of color removal of methylene blue plotted in figure (5) as a function of contact time. The initial concentration of 60 mg L^{-1} dye solutions methylene blue, 0.06 g of heat and acid treated toddy palm leaf powder (HTTPLP, ATTPLP) were used and then the solutions were equilibrated. The removal percent a few increases when contact time increases. After the equilibrium contact time (150 min), the percent removal is nearly constant. It was found that the percent removal of heat treated (82.11%) was less than that of acid treated (97.52%).

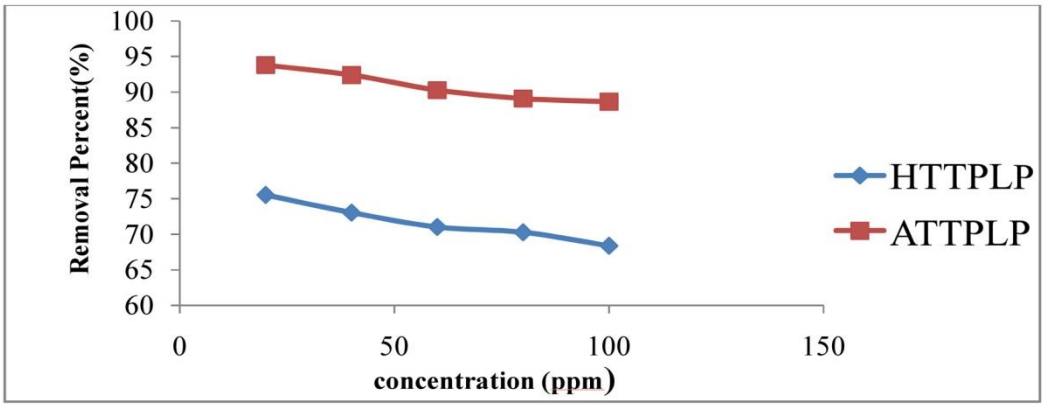


Figure (3) Removal percent of HTTPLP and ATTPLP as a function of initial concentration of methylene blue as 60 min contact time

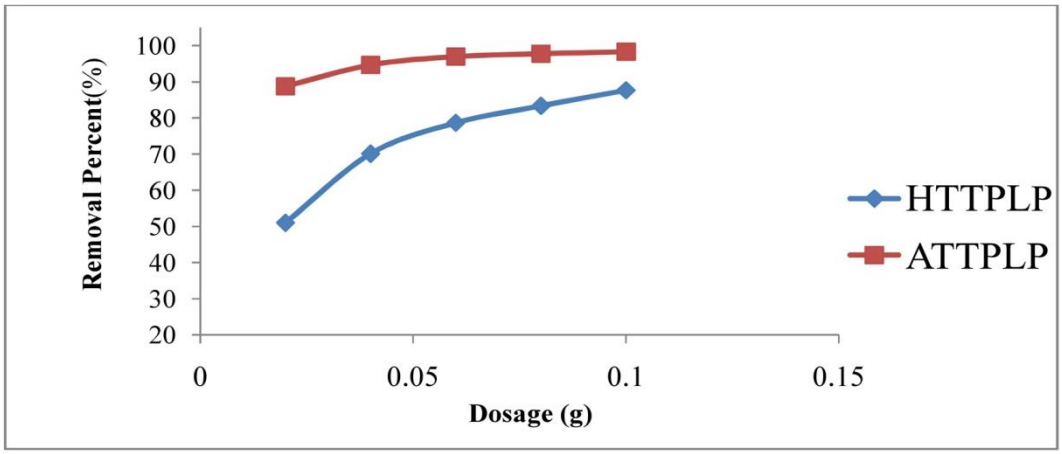


Figure (4) The Removal percent of methylene blue as function of dosage of HTTPLP and ATTPLP at 60 min contact time

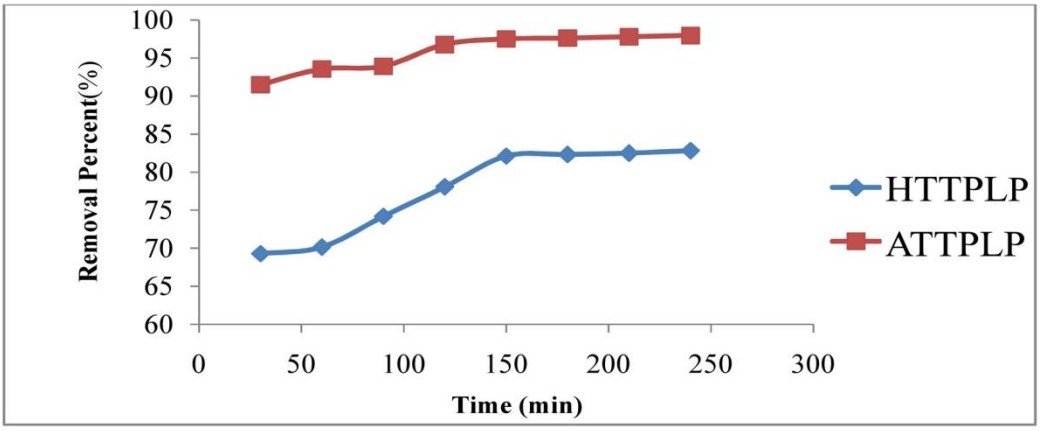


Figure (5) Removal percent of methylene blue on HTTPLP and ATTPLP as a function of contact time

In SEM analysis, silicon grease was coated on the brass stub at first. Then the sample was poured (spread) onto the grease and the stub was inserted into the ion sputter for gold coating on the sample. The stub with gold-coated specimen was placed in the sample holder and put into the Scanning Electron Microscope. The permanent records were obtained by photographing the sample crystals. figures SEM (6), (7) and (8) shows the micrograph of toddy palm leaf powder samples, Methylene blue with acid treated toddy palm leaf samples and 3 methylene blue with heat treated toddy palm leaf samples respectively.

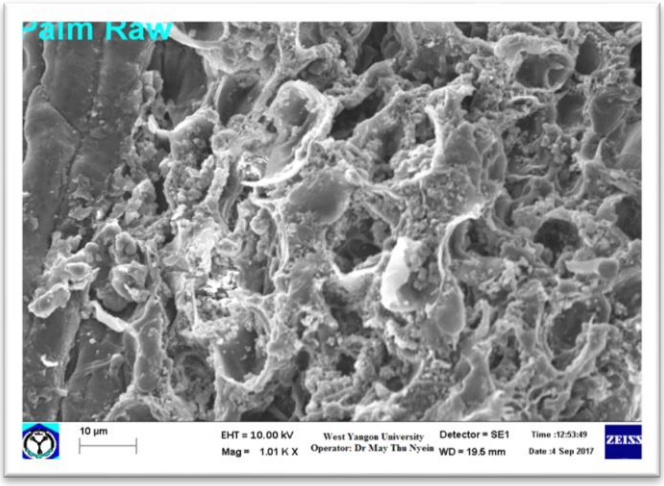


Figure (6) SEM micrograph of toddy palm leaf powder sample.

Figure (7) SEM micrograph of Methylene blue with acid treated toddy palm leaf powder sample

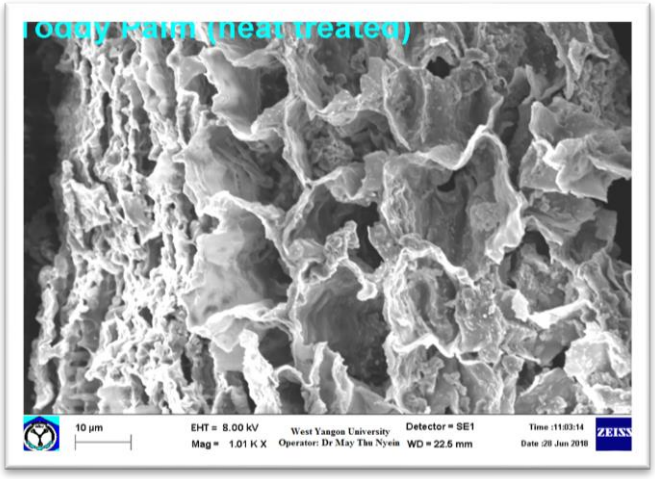


Figure (8) SEM micrograph of Methylene blue with heat treated toddy palm leaf powder sample

Conclusion

In this investigation, the toddy palm leaf, ground, dried, heat activated between 200℃ and 300℃ and acid treated with HCL (2%v/v) can be used successfully for the color removal of methylene under the optimized condition.

The characterization of prepared sample by SEM was able to reveal the surface morphology and spectral data of heat and acid treated toddy palm leaf powder.

In the effect of initial concentration, it was observed that the higher concentration becomes the fewer the available sites of adsorption and hence adsorption capacity also decrease.

In the effect of contact time, the adsorption capacity increase with increasing contact time and the equilibrium contact time reaches about 150 min.

In the effect of adsorbents dosage, the adsorption capacity increases with increasing dosage of sorbent.

So, the heat and acid treated toddy palm leaf powder samples in this investigation showed that it can be used as an effective biosorbent for the color removal of dye from aqueous solution. But the color removal percent of methylene blue (MB) by acid treated toddy palm leaf powder was greater than that of heat treated toddy palm leaf powder.

From these results, the advantages of this project are getting free from the difficulties of plucking and cleaning the toddy palm leaf. In contrast to, the color removal of methylene blue was excellent by the toddy palm leaf powder samples. It can be concluded that toddy palm leaf powder can be served as an eco-friendly sorbent material in the color removal of dye from industrial wastewater.

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References

Anielak, A.M., (1996). "Adsorption of Acid Dyes on Active Carbon", New York, J. *Environmental Science Research*, 51, 527-534.

Benaissa, H., (2005). "Removal of Acid Dyes from Aqueous Solution Using Orange Peel as a Sorbent Material", Egypt, Ninth International Water Technology Conference, 1175-1176.

Bayton, Ross P. (2007). "A revision of Borassus L. (Arecaceae)". *Kew Bulletin*. 62 (561-586).

Benguella, B. and H. Benaissa. (2002). "Cadmium Removal from Aqueous Solutions by Chitin: Kinetic and Equilibrium Studies". *Water research*, 36 (10), 2463-2474.

Malik, P.K ., (2003). "Use of Activated Carbons Prepared from Sawdust and Rice-husk for Adsorption of Acid Dyes", *A Case Study of Add Yellow 36, Dyes and Pigments*, 56(3), 239-249.

Ming, T. K., (2011). "Removal of Reactive Orange 16 (RO16) Using Chemically Modified Poneapples Peels", *Engineering and Science*, 4, 1-18.

Nabilah, A.L., Wong, Y.S., Ain, N. K. and Teong, H. Y., (2011). "Removal of Methylene Blue using Pineapple Powder of Adsorbent", Malaysia, International Conference, 3rd Edn., 352-917.

Sharifah Nhatasha Binti Syed Jaofar, (2006). "Adsorption Study-Dye Removal Using Clay", *University College of Engineering and Technology Malaysia*, 5, 1-26.

Tahir, H., Sultan, M. and Jahanzeb., (2008). "Removal of Basic Dye Methylene Blue by using Bioadsorbents Ultra Lactuc and Sargassum", *African Journal of Biotechnology*, 7(15),2649-2655.

Volseky B. (1990). *Biosorption and Biosorbents. In: Biosorption of Heavy Metals* Boston: CRC Press, 3-5.

Win Yin Cho Nwe, Kyaw Myo Naing and Tin Tin Aye, (2010). "Sorption Kinetics Study on the Color Removal Efficiency of Methylene Blue and Congo Red by Sawdust", *J. Myan. Acad. Arts and Sc*., 8(1), 121-130.