

PRELIMINARY ASSESSMENT ON THE ADSORPTION OF METHYLENE BLUE DYE IN WASTEWATER USING COCONUT LUMBER SAWDUST

Allyza Jean Cimafranca¹, Adrian Cueto¹, Karen Anne Desengano¹, Christelle Janer¹,
Maxiene Alex Mejia¹, Gizelle Balatico¹, and Louie Ian Mariano, RChE, MEN²

¹Psychology Program, College of Liberal Arts and Sciences

²Natural Science Area, College of Liberal Arts and Sciences

ABSTRACT

Color of water is the first indicator of contamination. It is, therefore, necessary to remove contaminants from wastewater before discharging it into water bodies as these are harmful, especially to aquatic life. Dyes from wastewater of textile and dying industries are currently one of the environmental problems, wherein increased concentration of these pollutants poses environmental water degradation. Using adsorption, this study tested the effectiveness of Coconut lumber sawdust, an indigenous waste product, as biosorbent in an artificially prepared methylene blue (MB) dye wastewater. The effect of the different initial concentration was also studied. Coconut lumber sawdust was treated with 0.01 M potassium hydroxide (KOH) and was activated at 180°C for two hours in an oven. The adsorption process included agitation through aeration. Filtered samples were analyzed using Perkin Elmer Lambda 40 UV-Vis spectrophotometer with the maximum wavelength of 665 nm. Results showed that the percent removal of MB using coconut lumber sawdust ranges from 68% to 81% that implies that coconut lumber sawdust is an effective biosorbent of MB. The equilibrium loading was found to increase as the initial concentration increases. The adsorption of MB is primarily because of the activation of the sawdust. During activation, the internal surface of the coconut lumber sawdust becomes more highly developed and extended by controlled oxidation of carbon atoms (Cameron Carbon Inc., 2009). Accessibility of the internal surface area is due to the network of pores opened as the coconut lumber sawdust was activated.

Keywords: Methylene blue, MB dye, Biosorption, Wastewater, Adsorption, Coconut lumber sawdust

INTRODUCTION

Wastewater includes water that is discharged from households, industrial sites and manufacturing plants. These wastewater are no longer considered fit for human consumption. Wastewater from manufacturing plants includes toxins and other harmful chemicals that were used for various products. An emerging source of wastewater is coming from the textile industry where concentration of dyes in the effluent water is high. Textile industry ranks first in the use of dyes in coloring fabrics.

The textile dyeing industry release large volumes of wastewater from different steps in the dyeing until the finishing processes. Dyeing industry discharge a large volume of effluents that are highly colored and heavily loaded with pollutants (Wang, Miaomiao, Huang & Liu, 2011). Color in the water is the first indicator of the contaminant and it has to be removed from wastewater before discharging it into water bodies because it may be very harmful especially to the aquatic life. This could interfere with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota, and interferes with gas solubility in water bodies. It could also be harmful to human beings because when dyes laden wastewater were directly discharged to municipal wastewater plants toxic carcinogenic breakdown products may be formed (Hamdoui, 2006). Moreover, even a concentration of 1.0 mg/L of dye could contaminate drinking water making it unfit for human consumption (Garg, Amita, Kumar & Gupta, 2004). There are different classifications of textile dyes that are being used particularly in our country. Acid dyes are used for dyeing nylon, silk and wool. Basic dyes are applicable for acrylic. Direct dyes are applicable for cotton, and linen. Disperse dyes are applicable for nylon and acetate. Methylene blue dye (MB) is a basic dye most commonly used in cotton, wood, and silk. Though methylene blue is not considered as strongly hazardous, exposure to it could still cause some harmful effects such as increased heart rate, vomiting, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Vadivelan & Kumar, 2005) as well as burning sensation in the eyes which may lead to permanent damage, mental confusion, high levels of methemoglobin in the blood and irregular breathing for short period of time (Ahmad et. al., 2009).

There are various methods or techniques on the removal of dyes from wastewater such as precipitation, coagulation, filtration, and chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photocatalysis. Chemical coagulation was commonly used to treat the wastewater containing disperse dye (Chu, 2001). These physical and chemical treatment processes are effective for dye removal however these also pose disadvantages such as its use of more energy, its complexity, expensiveness and its capability to produce other chemical wastes in the process of production. As an alternative, biological treatment processes for the treatment of textile wastewater were also studied such as bio-sludge, which is found to have high adsorption abilities on both dispersed dyes and organic matters (Sirianuntapiboon & Srisornsak, 2006). Previous studies also revealed that adsorption- a process where a solid is used for removing a soluble substance from the water- is one of the most effective and efficient methods for the removal of dyes in

The most common industrial adsorbents are activated carbon, silica gel, and alumina. Activated carbon is said to be the most efficient but it is also very costly. This is why a lot of researches looked into the use of industrial and agricultural waste products such as wood chips, wheat straw, corncobs, banana peels, coconut husk, tree bark, peanut skins, waste tire rubber, sawdust, leather waste and moss peat as alternatives. Other low-cost biosorbent for the removal of dye have been tested in various studies, too. These are Durian peel (Arami, Limaee, Mahmoodi & Tabrizi, 2005), Garlic peel (Hameed & Ahmad, 2008), Pomelo peel (Hameed, Mahmoud & Ahmad, 2007), chrome containing leather waste (Carpenter, Sharma, Sharma & Verma, 2013), organic clay (Khenifi, Bouberka, Sekrane, Kameche & Derriche, 2007), coconut husk (Tan, Ahmas & Hameed, 2007), and many more. Studies have shown that among the organic materials tested, sawdust is the most promising adsorbent in removing heavy metals, acid and basic dyes, and some other unwanted materials from waste water.

Sawdust is an organic waste solid product made from cutting, grinding and pulverizing wood. This exists widely in furniture manufacturing company and is either used as cooking fuel or as packing material. A number of studies on the adsorption of dyes using sawdust as adsorbent, specifically the use of methylene blue, were used in toxic salts, heavy metal, and oil from water (Shukla et al., 2002). The use of sawdust can be considered as one of the cheapest or low cost materials that can be used in removing contaminants in water. Since the Philippines has a rich lumber industry, it would be very advantageous for us to use sawdust in removing unwanted pollutants of water.

Literature suggests that sawdust from woods such as mahogany, beech, rubber wood, cedar and oak are commonly used in removing dyes in wastewaters. Interestingly, in the Philippines, the most popular and commonly used woods is the coconut tree. Given its availability and in relation to the study of coconut husk by Tan, Ahmas & Hameed (2007), this study focused on the use of sawdust from coconut lumber. The researchers also found limited studies about coconut lumber sawdust as biosorbent. It also seems to be the case that no study accounted on the use of coconut lumber sawdust in adsorption of methylene blue. Given these realities, this study aimed to test the effectiveness of sawdust from the Coconut lumber as biosorbent of dyes from wastewaters, particularly methylene blue. In addition, this study aimed to examine the sorption efficiency of coconut lumber sawdust in removing methylene blue dye from wastewater at varying initial concentration of the dye in wastewater. Several limitations, however, were accounted for this study. First, this study

only focused on the effect of the concentration of the wastewater to the adsorption. Second, the use of coconut lumber sawdust as biosorbent was only tested in methylene blue dye.

Sawdust from Coco lumber is a very low-cost material and is an abundant organic material here in Philippines. This study found another efficient solution on removing dye from wastewater. More so, it maximizes the use of a supposed to be waste products from the wood industry. This present study would also be able to extend past researches of sawdust as an adsorbent for dye removal in wastewaters by using another kind of material that has not been that explored yet. This would benefit our own country because it uses a locally available material unlike previous studies which used imported materials.

MATERIALS AND METHOD

Preparation of the Biosorbent

Coconut lumber sawdust was obtained from a local Coco lumber manufacturer in Caloocan City. As a dehydration agent, the materials were soaked with 0.01 M potassium hydroxide (KOH) with the ratio of 1:1 for two hours. This helped produce and activate pores in the coconut lumber sawdust (Tan, Hameed & Ahmad, 2008). The coconut lumber sawdust was heated using a baking oven at 180°C (Valix & Mckay, 2004) for another two hours to activate the pores and to further remove the water and moisture content in the coconut lumber sawdust. The resulting material was then stored in an airtight container before the adsorption process.

Preparation of Artificial dye wastewater

A 400 ppm methylene blue stock solution was prepared by diluting 0.4 g of methylene blue powder with 1 liter of distilled water. Experimental solutions of the desired concentration were obtained by successive dilutions.

Adsorption Procedure

The sorption characteristics were carried out at five varying concentrations of the artificial methylene blue dye wastewater: 100 ppm, 150 ppm, 200 ppm, 250 pmm and 300 ppm (Garg, *Antorcha Vol. 3 No. 1 (March 2016)*

Amita, Kumar & Gupt, 2004). A 2.4 g of the biosorbent was added into each 600 mL solution. The solutions were agitated through aeration from a gyratory water bath shaker procedure. Aeration is the process of bringing water and air into close contact by introducing small bubbles of air and letting them rise through the water which helps in removing undesirable gases and other constituents that could interfere with the treatment process. Thin tube hose connected to the water pumps were placed inside each container of the samples for 12 hours. After adsorption, it was filtered using Whatman filter paper no. 40. Afterwards, the samples were stored in the refrigerator before the analysis. The concentration of methylene blue in the filtered solution after the adsorption was determined using the Perkin Elmer Lambda 40 UV-visible spectrophotometer set at a wave-length of 665 nm, maximum absorbance (Hamdaoui, 2006).

The efficiency of the adsorption was calculated using this equation:

$$\%_{adsorption} = \frac{C_i - C_{eq}}{C_i} \times 100$$

where:

C_i = initial concentration of the adsorbate (ppm)

C_{eq} = final equilibrium concentration of the adsorbate (ppm)

The equilibrium loading, or the amount adsorbed per unit mass of adsorbent was calculated using this equation:

$$q_e = V (C_i - C_{eq}) / m$$

where:

C_i = initial concentration of the adsorbate (ppm)

C_{eq} = final equilibrium concentration of the adsorbate (ppm)

V = volume of the solution (L)

m = mass of the adsorbent (g)

RESULTS

Effects of Varying Initial Concentration

The effect of varying the initial concentration in the adsorption of methylene blue dye wastewater using coconut lumber sawdust was examined. Table 1 shows the initial concentration, final concentration, equilibrium loading and the percent adsorption of methylene blue. Based from the results of the study, the percent removal of methylene blue using coconut lumber sawdust ranges from 68% to 81%. This implies that coconut lumber sawdust is an effective biosorbent of methylene blue. The optimum concentration for the adsorption is 100 ppm.

Table 1: Equilibrium loading and percent adsorption of methylene blue with varying initial concentration

C _{in} ppm	C _{eq} ppm	q mg/g	% adsorption
100	19	20.25	81%
150	40	27.5	73%
200	68	33	68%
250	68	45.5	72.8%
300	75	56.25	75%

Figure 1 shows that as the initial concentration increases, the equilibrium loading also increases. This means that the diffusion of the contaminant, methylene blue, in the coconut lumber sawdust is greater as the initial concentration of methylene blue increases.

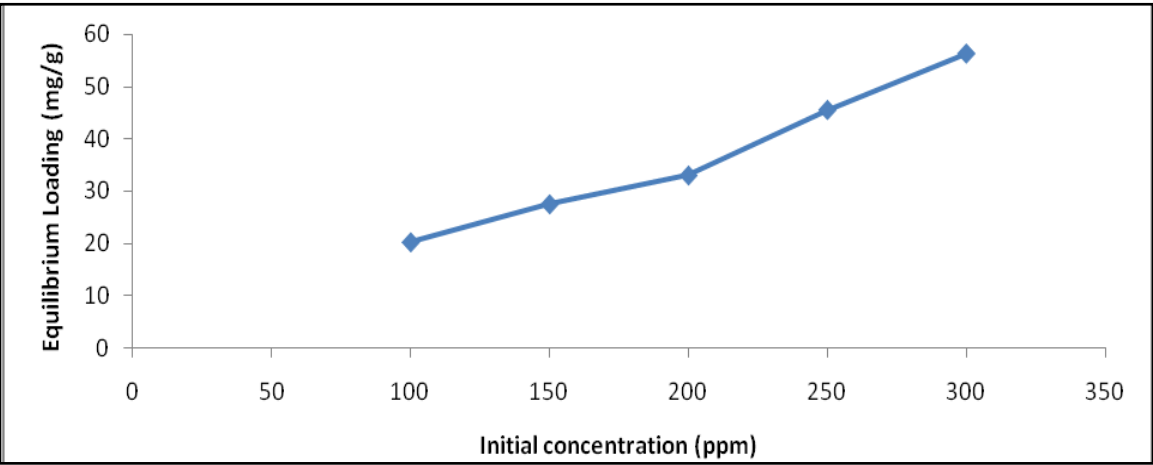


Figure 1: Equilibrium loading and initial concentration

DISCUSSION

The current study found out that activated coconut lumber sawdust is an effective biosorbent of methylene blue dye in wastewater. It is evident that the solutions have significant change in color from dark blue to light blue. Also, based from the analysis of the solutions using UV Visible Spectrophotometer, as compared to the standard solution, the concentration was found to be lessened because of the adsorption of methylene blue dye by the activated sawdust. Methylene blue dye was effectively adsorbed by the activated sawdust because of its adsorbent properties.

During activation, the internal surface of the coconut lumber sawdust becomes more highly developed and extended by controlled oxidation of carbon atoms (Cameron Carbon Inc., 2009). Adsorption potential exist because the internal surface area became accessible to the passage of a fluid or vapor. Accessibility of the internal surface area is due to the network of pores opened as the coconut lumber sawdust macropores, mesopores, and micropores were activated. The macropores provided a passageway to the particle's interior and to the micropores but did not contribute substantially to the interior surface area. The mesopores, on the other hand, were the secondary channels formed in the walls of the macropore structure. Lastly, the micropores were responsible for the large surface area of activated carbon particles and are created during the activation process.

The study further revealed that it is in the micropores that adsorption largely takes place. Thus, the research argues that two main parameters are relevant to the performance of the activated coconut lumber sawdust: the surface area and the pore volume or structure. The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material that can be adsorbed, assuming a suitable molecular size (Lartey, Acquah, Nketia, 1999). In the adsorption process, molecules are held by the carbon's surface by weak Van Der Waals Forces resulting to an intermolecular attraction (Cameron Carbon Inc., 2009).

CONCLUSIONS

Coconut lumber sawdust was found to be an effective biosorbent for methylene blue dye in wastewater. This is primarily because of the activation of the sawdust. The equilibrium loading was found to increase as the initial concentration increases. The percent adsorbance of methylene blue ranges from 68% to 81%. Results are in synch with other studies that found coconut products to be effective biosorbent of Methylene blue such as coconut shell (Sodeinde et al., 2013) and coconut Fibre (Wong et al., 2013).

RECOMMENDATIONS

It is suggested that for further studies, experiments also focused on other factors such as the particle size, amount of biosorbent, temperature, pH level, and contact time, which are deemed to affect adsorption. In addition, future studies should also study the effectiveness of the adsorption of coconut lumber sawdust in other chemicals aside from methylene blue.

REFERENCES:

- Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M., & Hashim, R. (2009). Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. *Journal of Hazardous Materials*, 170, 357-365.
- Banat, I.M., Nigam, P., Singh, D., & Marchant, R. (1996). Microbial decolourization of textile dyes containing effluents: a review. *Bioresources Technology*, 58, 217–227.
- Batzias, F., & Sidiras, D. (2004). Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems. *Journal of Hazardous Materials*, Vol. 114 (1), 167-174.
- Batzias, F., & Sidiras, D. (2007). Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems, *Biosource Technology*, Vol. 98 (6). 1208-1217.
- Batzias, F.A., & Sidiras, D.K. (2007). Simulation of dye adsorption by beech sawdust as affected by pH. *Journal of Hazardous Materials*, 141(3), 668-679.
- Cameron Carbon Incorporated (2006) Activated Carbon: Production, Structure, and Properties. *Activated Carbon and Related Technology*. Retrieved October 5, 2013, from http://www.cameroncarbon.com/documents/carbon_structure.pdf
- Elhami, S., Faraji, H., & Taheri, M. Removal of neutral red dye from water samples using adsorption on bagasse and sawdust. *J.Chem.Soc.Pak.*, 34(2), 269-272.
- Foo, K.Y., & Hameed, B.H. (2012) Mesoporous activated carbon from wood sawdust by K₂CO₃ activation using microwave heating. *Bioresource Technology*, 111, 425–432. <http://dx.doi.org/10.1016/j.biortech.2012.01.141>
- Garg, V.K. , Amita, M., Kumar, R. & Gupta, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and Pigments*, 63 (3), 243-250.

- Hamdaoui, O. (2006). Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials*, B135, 264–273.
- Hameed, B.H., Ahmad, A.L., & Latiff, K.N.A. (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and Pigments*, 75, 143-149.
- Kamal, et. Al (2011). Acid Blue 25 adsorption on base treated shorea dasyphylla sawdust: kinetic, isotherm, thermodynamic and spectroscopic analysis. *Journal of Environmental Sciences*, 24(2), 261–268.
- Lartey R. B., Acquah F. and Nketia K. S. (1999). “Developing National Capability for Manufacture of Activated Carbon from Agricultural Wastes”, The Ghana Engineer. www.researchgate.net/publication/264874176_DEVELOPING_NATIONAL_CAPABILITY_FOR_MANUFACTURE_OF_ACTIVATED_CARBON_FROM_AGRICULTURAL_WASTES
- Malik, P.K. (2004). Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, B113, 81–88.
- Mohd Din, A., Hameed, B.H., & Ahmad, A. (2008). Batch adsorption of phenol onto physiochemical-activated coconut shell. *Journal of Hazardous Materials*, 161, 1522–1529.
- Prakash-Kumar, B.G., Shivakamy, K., Miranda, L.R. & Velan M. (2006). Preparation of steam activated carbon from rubberwood sawdust (*Hevea brasiliensis*) and its adsorption kinetics. *Journal of Hazardous Materials*, 136 (3), 922–929. <http://dx.doi.org/10.1016/j.jhazmat.2006.01.037>
- Sodeinde, O., & Eboreime, U. (2013). Adsorption of textile wastes containing Methylene blue & Congo red using activated carbon produced from coconut shell. *International Journal of Computational Engineering and Management*, Vol. 16 (5), 2230-7893.
- Tan, I., Ahmad, A., & Hameed B. (2008). Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium , kinetic and thermodynamic studies. *Journal of Hazardous Materials*, 154, 337–346.
- Vadivelan V., & Vasanth, K. (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J Colloid Interface Science*, 90-100.
- Valix, M., Cheung, W., & McKay, G. (2004). Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. *Chemosphere* Vol. 56 (5), 493-501.

Wong, Y., Senan, M., & Atiqah, N. (2013). Removal of Methylene Blue and Malachite Green Dye Using Different Form of Coconut Fibre as Absorbent. *Journal of Basic and Applied Science*, 2013, 9, 172-177.