Kinetics and Isotherm Studies of Methylene Blue Dye Adsorption onto Microwaved Mahogany Fruit Husk Activated Carbon

Bryan John A. Magoling*, Angelica A. Angeles-Macalalad

Abstract— There is a great demand for the development of more economical and environmentally friendly methods for producing activated carbons. Of such methods, the application of microwave treatment during activation process has shown to produce desirable surface morphology for adsorption applications. In this study, activated carbon was produced from mahogany fruit husk through chemical impregnation with phosphoric acid followed by microwave thermal treatment. Kinetics of the adsorption process was studied using first-order and second-order-kinetics models while the Langmuir and Freundlich models were used to study the adsorption isotherm of the microwaved MFHAC. The Adsorption of MB on microwaved MFHAC fitted the Langmuir isotherm and followed the pseudo-second-order kinetic model. Analysis of the surface morphology of the microwaved MFHAC revealed the presence of highly porous structure. Overall, the process via microwave irradiation produces highly adsorbing AC at a significantly lesser heating time and with lower energy consumption. Hence, microwave-assisted activation of mahogany fruit husk can be used for the efficient removal of methylene blue in aqueous solutions.

Index Terms— Adsorption, Activated carbon, Isotherm studies, Kinetics studies, Mahogany fruit husk, Microwave-thermal treatment, Methylene blue dye removal; Simulated waste water

1 INTRODUCTION

TEXTILE industries generate wastewater which can contain a number of toxic contaminants. The effluent from the textile industries contains different dyes. These dyes impose toxic, carcinogenic, mutagenic, and teratogenic effects to human beings and to other living organisms [1]. Furthermore, dye contaminations in water tend to prevent light penetration and affects photosynthesis [2-3]. Therefore, its removal from aquatic wastewater is of great interest.

There are numerous ways of color removal from waters and wastewaters such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, and reverse osmosis [4-5]. The adsorption process, which is based on the transfer of pollutants from the solution to the solid phase, is known as one of the efficient and general wastewater treatment method [6]. It is very effective in textile wastewater treatment considering it is cheap, sludge free, and can completely remove even minute amount of dyes in water [7].

The surface structure of activated carbon consists of different sizes of pores including micropores, mesopores and macropores. The importance of measuring the surface area and other characteristics, such as micropore volume, total pore volume and average pore size of an adsorbent is the relative dependence of its adsorption capacity to these properties [8]. Adsorption, defined as a surface phenomenon, can be physical and chemical adsorption depending on the type of attractions existing between adsorbate and adsorbent. Physical adsorption or physisorption happens when the force of attraction existing between adsorbate and adsorbent are weak Vander waals forces of attraction. It occurs with formation of multilayer of adsorbate on adsorbent. It has a low enthalpy of adsorption that happens at low temperature below boiling point of adsorbate. On the other hand, chemical adsorption or chemisorption is a process that takes place when the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond.

Kinetics and Isotherm explain adsorption which show how much solute can be adsorbed by the adsorbent at a given temperature. Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and remained in solution at equilibrium at constant temperature [9]. Adsorption isotherms are important to predict how adsorbates will interact with adsorbents. The Langmuir and Freundlich isotherms are the most commonly used for solid-liquid phase. These isotherms relate the amount of colour adsorbed per unit weight of the adsorbent to the colour concentration at equilibrium. Freundlich isotherm model describes nonideal sorption onto heterogeneous surfaces involving multilayer sorption [5].

The present study aimed to investigate the adsorption capacity of mahogany fruit husk activated carbon prepared using microwave oven for the removal of methylene blue. The pseudo-first order and pseudo-second order models are used to correlate the adsorption kinetics data. Adsorption isotherms were determined and modeled with Langmuir and Freundlich isotherms.

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2 METHODS

2.1 Aqueous solution

A stock solution was prepared by dissolving 1g of methylene blue (MB) powder in 1L of distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations.

2.2 Preparation of activated carbon

Mahogany fruit husks were obtained from Batangas City, Philippines. They were rinsed thrice with distilled water and then dried in an oven at 105°C for 24 h to remove moisture. The samples were ground and sieved to a particle size between 2.0 mm and 4.75 mm. Carbonization was carried out by loading the dried precursor into a stainless steel vertical tube reactor placed in a tube furnace for 1h under purified nitrogen flow. Phosphoric acid (H_3PO_4) was used to activate the char via the chemical activation method. The carbonized MFH sample was soaked in 40% (v/v) H_3PO_4 with an impregnation ratio of 1:2 (weight of char: weight of H_3PO_4) for 2 hours at 80°C. Afterwards, the samples were filtered using a vacuum pump and oven dried overnight at 105°C. Activation of impregnated char was carried out using a modified commercial microwave with a frequency of 2.45 GHz at different power level ranging from 140 W for 5.5 mins under a nitrogen flow of 300 cm^3/min. The sample was then cooled to room temperature under nitrogen flow and washed with hot deionized water and 0.1 M HCl until the pH of the washed solution ranged from 6 to 7.

2.3 Batch equilibrium studies

In each flask, we placed 100 mL of the aqueous solution with varying initial MB concentrations. 0.30 g of the prepared AC sample was added to each flask, which were then kept in an isothermal shaker at 200 rpm and 30°C. After agitation, the solid was removed by filtration through a Whatman #1 membrane filter paper. The filtrates were collected in clean, dried bottles, and were prepared for analysis using a UV-Vis spectrophotometer. The sorbed dye concentrations were obtained from the difference between the initial and final dye concentrations in solution. The percentage removal at equilibrium was calculated as following equation:

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad \text{eq. 1}$$

where C_o and C_e are the liquid-phase concentrations at initial state and at equilibrium (mg/L), respectively. The amount of dye adsorbed per unit mass of adsorbent at equilibrium conditions, qe (mg/g), was calculated by equation:

$$q_e = \frac{(C_p - C_e)V}{W} \quad \text{eq. 2}$$

where qe (mg/g) is the amount of solute adsorbed per unit weight of adsorbent; C_o and C_e (mg/L) are the liquid-phase concentrations of adsorbate at initial and equilibrium conditions, respectively; V (L) is the volume of the solution; and W (g) is the mass of adsorbent used.

2.4 Characterization of prepared activated carbon

The surface area, pore volume and average pore diameter of the samples were determined by using Quantachrome volumetric adsorption analyzer. The BET surface area was measured from the adsorption isotherm using Brunauer–Emmett–Teller equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the samples was examined using a scanning electron microscope.

3 RESULTS AND DISCUSSIONS

3.1 Kinetics studies

Adsorption kinetics is of great significance in evaluating the performance of a certain adsorbent and in gaining insight into the underlying mechanisms. Kinetic modelling allows for the investigation of important adsorbent characteristics like mechanism of adsorption and the potential rate-controlling processes, mass transfer and chemical reaction [10]. Table 1 shows the fitting of the MB adsorption kinetic data of microwaved MFHAC into the pseudo-first and pseudo-second order models, respectively. The pseudo-first-order model is illustrated as following equation:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{K_1 t}{2.303} \quad \text{eq. 3}$$

A pseudo-second-order model is described as following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{eq. 4}$$

where qe and qt (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively, k_1 (1/h) and k_2 (g/mg h) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order models, respectively and t (h) is the contact time. The values of K_1 and R^2 obtained from the plot for adsorption of methylene blue on the microwaved MFH-AC are reported in Table 1.

TABLE 1
PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER KINETIC MODEL PARAMETERS FOR 50 PPM METHYLENE BLUE SOLUTION

Kinetic Model	Parameters	Values
Pseudo – first order	q_e exp (mg/g)	145.734
	q_e calc (mg/g)	483.91
	K_1 (min^{-1})	0.0362
	R^2	0.7795
Pseudo – second order	q_e exp (mg/g)	145.734
	q_e calc (mg/g)	181
	K_2 (g/mg.min)	0.02689
	R^2	0.9976

The R^2 value (0.7795) obtained for the pseudo-first-order model was not high and the experimental q_e did not agree with the

calculated value obtained from the linear plot. This finding shows that the adsorption of methylene blue on the adsorbent does not follow a pseudo first order kinetic model. A high correlation coefficient (R^2) value was obtained from the linear plot of t/qt versus t for pseudo second-order equation. The closeness to unity of the obtained correlation coefficient (0.9976) for the second-order indicates that the adsorption of methylene on microwaved MFHAC fits this model well and that the adsorption process is controlled by chemisorption. There was also a good agreement between the experimental and calculated q_e values, further affirming the fit of the model.

Chemisorption occurs as strong, short-ranged bonding between adsorbate and substrate. Unlike physiosorption which happens due to weak van der Waals attraction between adsorbate and substrate resulting to multi-layered adsorption, chemisorption can happen via covalent, ionic, or metallic bonding resulting to a monolayer adsorption process.

Taking into consideration the abovementioned surface characteristics of the microwave-irradiated MFHAC, the following mechanisms are proposed for the chemisorption of MB onto the surface of the adsorbent:

1. Electrostatic interactions between the deprotonated phenolic or carboxyl groups and the cation N^+ of the MB (Olivella, Fiol, de la Torre, Poch, & Villaescusa, 2012)
2. n-pi interactions between deprotonated carboxyl groups ($-COO^-$) of the sorbents as n-donors with the pi-acceptor sites of the aromatic ring of the MB (Keiluweit & Kleber, 2009)
3. cation-pi interactions: the cationic center N^+ of MB can make favorable interactions with the pi-electron cloud of aromatic side chains (Aschi, Mazza, & Di Nola, 2002)
4. pi-pi interactions between pi aromatic ring donors of MB and pi acceptor groups in the sorbents (Keiluweit & Kleber, 2009)

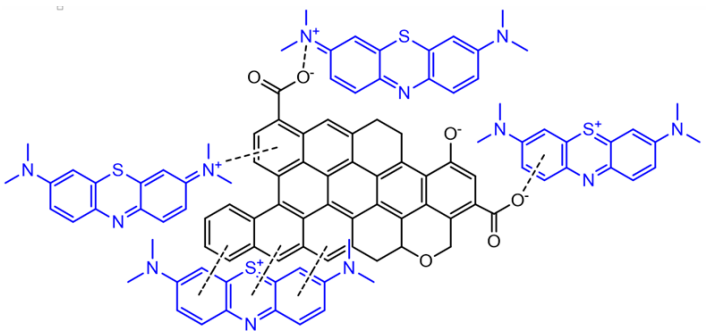

Fig 1. Proposed interactions of methylene blue onto the surface of the microwaved MFHAC

3.2 Adsorption studies

In this study, two widely used isotherm models, Langmuir model and Freundlich model were employed to describe the adsorption process. The Langmuir model is based on the assumption that adsorption energy is constant and independent of surface coverage. Maximum adsorption occurs once the surface is covered by a monolayer of adsorbate [11]. The linear form of the Langmuir isotherm equation is given as equation:

$$\frac{1}{(q_e)} = \frac{1}{QbC_e} + \frac{1}{Q} \quad \text{eq. 5}$$

where C_e (mg/L) is the equilibrium liquid-phase concentration of dye, q_e (mg/g) is the equilibrium uptake capacity, Q (mg/g) is the Langmuir constant related to adsorption capacity, and b (L/mg) is the Langmuir constant related to the energy of sorption, which quantitatively reflects the affinity between the sorbent and the sorbate. The equilibrium data were fitted to the Langmuir isotherm by plotting $1/(q_e)$ versus $1/C_e$ using a straight line. Q was evaluated from the intercept and b was determined from the slope. The characteristics of the Langmuir isotherm can be expressed using the equilibrium parameter R_L [12] equation:

$$R_L = \frac{1}{(1 + bC_o)} \quad \text{eq. 6}$$

where b is the Langmuir constant and C_o is the initial pollutant concentration (mg/L). The value of R_L indicates whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for the adsorption of MB on the MFHAC was 0.06751 indicating that the adsorption is a favorable process. By the courtesy of Langmuir isotherm model, the maximum adsorption capacity (q_{max}) of MB on microwaved MFHAC was calculated to be 400 mg/g at 30°C.

The Freundlich model is based on sorption on a heterogeneous surface of varied affinities. The linear form of Freundlich model is given as equation:

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad \text{eq. 7}$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the adsorbate concentration, K_f (m/g)(L/mg)$1/n$ is the Freundlich constant related to adsorption capacity, and $1/n$ is the Freundlich constant related to sorption intensity of the sorbent.

Equilibrium isotherm constants and correlation coefficients obtained from linear fits of Langmuir and Freundlich are given in Table 2.

TABLE 2
CONSTANTS OF LANGMUIR AND FREUNDLICH ISOTHERMS

Langmuir constants			Freundlich constants		
K_L	R_L	R^2	K_f	$1/n$	R^2
0.12315	0.06751	0.9933	88.9405	0.3299	0.7884

Taking account of the correlation coefficients (R^2) of both models, the related coefficient R^2 of Langmuir equations is significantly higher than that of Freundlich equation, confirming the occurrence of monolayer adsorption of methylene blue onto the internal and external surface of microwave irradiated MFHAC. Furthermore, the slope of $1/n$ in the Freundlich graph is less than 1 which indicates a normal Langmuir isotherm.

3.3 Characterization of microwaved MFHAC

Table 3 shows the surface and pore characteristics (BET surface area, total pore volume, and mean pore radius) of the derived MFHAC samples. As can be seen from the table, the microwave irradiated MFHAC have relatively the same surface area of m^2/g.

The average pore diameters for the microwave irradiated MFHAC was found to be 3.4072 nm. This average pore diameter indicates that the AC prepared are in the mesopore region (2-50 nm diameter), according to the International Union of Pure and Applied Chemistry. The mesoporous characteristic of the produced ACs is suitable for methylene blue adsorption because the MB molecules have a minimum molecular cross-section of 0.8 nm, and the minimum pore diameter that the MB molecule can enter was estimated to be 1.3 nm. Therefore, MB can enter most mesopores and the largest micropores [13].

TABLE 3
SURFACE AND PORE CHARACTERISTICS OF MICROWAVED MFHACS

Heat treatment used	Surface Area, S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Ave. Pore Diameter (nm)
Microwave	330.754	0.244	3.4072

Fig. 2 shows the SEM image of the derived microwaved MFHAC prepared under optimum conditions. It can be found that the microwave irradiated sample has well developed and uniform surface with an orderly pore structure. The presence of deep macropore hole structures on the microwave irradiated MFHAC samples suggests a well-developed pore structure [13]. With this developed pore structure, there is a higher probability that methylene blue can be trapped and adsorbed onto the surface of the microwaved MFHAC.

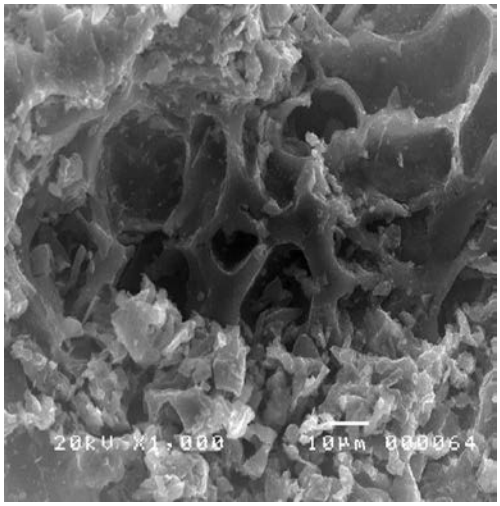

Fig. 2. SEM image of the optimized microwaved MFHAC at 1,000x magnification

4 CONCLUSIONS

Optimization of MB removal from solution using MFHAC prepared by microwave was investigated. Integration of microwave heating promotes porosity development. The adsorption data fitted the Langmuir isotherm while Adsorption kinetics followed the pseudo-second-order, demonstrating that chemisorption is the rate-controlling step during MB adsorption. Overall, the introduced process via microwave provides a faster and low energy consuming alternative to produce AC of comparable quality to conventionally prepared ACs.

5 REFERENCES

[1] Konicki, W., Sibera, D., Mijowska, E., Lendzion-Bielun, Z., Narkiewicz, U. (2013). Equilibrium and kinetic studies on acid dye acid red 88 adsorption by magnetic $ZnFe_2O_4$ spinel ferrite nanoparticles. J. Colloid Interf. Sci., 398:152-160

[2] S. Banerjee, M.C. Chattopadhyaya. Adsorption characteristics for the removal of a toxic dye tartrazine from aqueous solutions by a low cost agricultural by-product. Arabian Journal of Chemistry, 10 (2017), pp. S1629-S1638

[3] S. Hajati, M. Ghaedi, F. Karimi, B. Barazesh, R. Sahraei, A. Daneshfar. (2014). Competitive adsorption of direct yellow 12 and reactive o12 on ZnS:Mn nanoparticles loaded on activated carbon as novel adsorbent.J. Ind. Eng. Chem., 20:564-571

[4] Aljeboree, A. M., Alshirifi, A. N., Alkaim, A. F. (2017). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. Arabian Journal of Chemistry, 10:S3381-S3393

[5] Gumel, S.M. and Ismail, S. (2015). Use of Activated Carbon Derived from Maize Cob and Mahogany Seed Shell for the Removal of Colour from Textile Effluent. ChemSearch Journal 6(2):55 – 61

[6] Ghaedi, M., Sadeghian, B. Pebdani, A.A., Sahraei, R., Daneshfar, A. Duran, C. (2012). Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. Chem. Eng. J., 187:133-141

[7] Yakubu, M.K, Gumel, M.S and Abdullahi A.M. (2008). Use of Activated Carbon from date seeds to treat textile and tannery effluents. African Journal of Science and Technology, 9(1): 39 – 49.

[8] Taňala, F. N. A. (2011). The Effect of Surface Modification of Coconut Shell-Based Activated Carbon on Methomyl Adsorption.

[9] Ashish S. Sartape, Suryakant A. Patil, Sandip K. Patil, Suresh T. Salunkhe & Sanjay S. Kolekar (2015) Mahogany fruit shell: a new low-cost adsorbent for removal of methylene blue dye from aqueous solutions, Desalination and Water Treatment, 53:1, 99-108, DOI: 10.1080/19443994.2013.839404

[10] Hameed B (2009). Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard. Mater. 161, 753–759.

[11] Langmuir (1918). The adsorption of gases on plane surfaces of glass mica and platinum, J. Am. Chem. Soc. 40, 1361–1403.

[12] T.W. Webi, R.K. Chakravort (1974). Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20, 228–238.

[13] Hesas, R., Daud, W., Sahu, J., & Arami-Niya, A. (2013). The effects of a microwave heating method on the production of activated carbon from agricultural waste: a review. Journal of Analytical and Applied Pyrolysis, 100, 1-11.