Journal of Population Therapeutics & Clinical Pharmacology

RESEARCH ARTICLE
DOI: 10.53555/qpmbwh85

ADSORPTION OF METHYLENE BLUE DYE USING BIOCHAR DERIVED FROM *AEGLE MARMELOS* IMPREGNATED WITH VARIOUS ACIDS

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Abstract
The preparation of activated carbon from *Aegle Marmelos* fruits shell, a biomass solid waste, required the use of three distinct acids as an activator. For the purpose of removing the cationic dye methylene blue (MB) from an aqueous solution, the activated carbon that had been treated with sulphuric acid served as the best low-cost adsorbent. Variations in adsorbent dose (0.1–1g/L), initial dye concentration (50–250 mg/L), and contact time (10–60 min) were used to evaluate MB adsorption from an aqueous solution under equilibrium and kinetic conditions in batch mode. The Freundlich model did not fit the equilibrium data as well as the Langmuir isotherm model did. Compared to hydrochloric acid and phosphoric acid, sulphuric acid-treated carbon had the highest adsorption capacity. The pseudo-second order (PSO) kinetic gave a good description of the results of the kinetic uptake.

Keywords: activated carbon; adsorption; *Aegle Marmelos*; methylene blue; sulphuric acid; hydrochloric acid, phosphoric acid and chemical activation

Introduction

The textile, paper, pulp mill, leather, dye synthesis, printing, food, and plastics industries all make use of dyes frequently. Removal of organic dyestuffs from wastewater has received a lot of attention over the past few decades due to the fact that many of them are harmful to humans and toxic to microorganisms (Vargas et al., 2011). The majority of these dyes pose serious threats to the ecological system because they are regarded as toxic and have the potential to cause cancer, making the water hostile to aquatic life (El Qada et al., 2006). Dying industry effluents are one of the most difficult wastewaters to treat because of their high chemical and biological oxygen requirements, high concentrations of toxic compounds in the suspended solids, and colour, which is the first contaminant that humans recognize (Gao et al., 2013).

Methylene Blue is a thiazine (a cationic dye) that is mostly used to colour paper, make temporary hair colour, dye cotton, wool, and other textiles, among other things. Despite the fact that MB isn't viewed as an exceptionally poisonous colour, it can uncover extremely hurtful consequences for living things. In humans, breathing difficulties, vomiting, diarrhoea, and nausea can occur after inhalation (Khichi et al., 2011).

Biological treatment, ion-exchange, coagulation/flocculation, micro electrolysis, the Fenton process, advanced oxidation processes, ozonisation, adsorption, membrane filtration, photocatalysis, and other

combined techniques are the main treatment technologies for effectively removing dyes from dye-containing wastewater (Liu et al., 2019).
The expense of water cleansing by these innovations, with the exception of adsorption, goes from 10 to 450 US$ per cubic meter of treated water. In contrast, the cost of treating water with activated carbon adsorption ranges from $5 to $200 per cubic meter. In addition, adsorption is thought to be the best method for treating wastewater because of its ease of use and wide range of applications (El-Bery et al., 2022).
Various plant materials, including coconut husk, palm fibre, water fern, peat moss, duck weed, wheat bran, *Rhizopus nigricans*, modified corn starch, modified onion skins, saw dust, water lettuce, *Alterneuthera triandra, Citrus aurantium, Musa paradiasca*, and *Achras sapota*, have been the subject of numerous investigations by researchers (Bhati and Singh, 2012).
As per our awareness there is no study that compared the effects of various acid activation on the surface texture properties of AC derived from *Aegle Marmelos* fruit shell for the adsorption of methylene dye pollutants. The best models that provide a more accurate description of the adsorption process were investigated using adsorption kinetics and isotherms.

Materials and Methods

Preparation and characterisation of activated carbon

Locally, dry *Aegle Marmelos* fruit shell was washed, dried, and crushed to the desired mesh size as a raw material for the preparation of activated carbon. A portion of the produced powder was soaked with 50% concentrations of three different acids (sulphuric acid, phosphoric acid, and hydrochloric acid) at an impregnation ratio of 1:1 (Acid: Material) after the raw material was first pyrolyzed and then carbonized for one hour at 700 °C. After being dehydrated overnight at 105°C in an oven, the mixture was pyrolyzed in a furnace at 850°C and activated for two hours. The activated product was then cooled to room temperature and washed with deionized water to remove any remaining chemical. The sample was then dried in a hot air oven set to 105 degrees Celsius.

Batch equilibrium studies

Adsorption isotherms were carried out in a set of 250 ml flasks containing dye solutions (50 ml) of varying initial concentrations (50–250 mg/L). In order to achieve equilibrium in the solid solution mixture, 0.1 g of activated carbon of equal mass was added to dye solutions and kept in an isothermal shaker at 30 °C for one hour. Another set of Erlenmeyer flasks with the same dye concentration but no activated carbon was used as a blank and went through the same procedure. 0.1 mol l-1 sodium hydroxide or a few drops of diluted hydrochloric acid were added to bring the pH to 7. After that, the flasks were taken out of the shaker, and the dye concentration in the solution was checked. Before analysis, the samples were filtered to prevent carbon fines from interfering with the results. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = (C_0 - C_e)V/ W$$

Where C_0 and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Results and Discussion

Effect of contact time

At constant carbon concentrations and doses, the adsorption data for MB removal versus contact time are depicted in Figure 1. The colour evacuation rate expanded with the expansion in contact time and stayed steady after an equilibrium time was reached. As can be seen in Figure 1, the absence of active sites on the adsorbent causes the rate of adsorption to slow down after it reaches a certain point during the contact time. Compared to hydrochloric acid and phosphoric acid, which adsorb 61% and 67 % of MB, sulphuric acid treated carbon achieved the highest maximum adsorption of 70 % of MB after 50 minutes.

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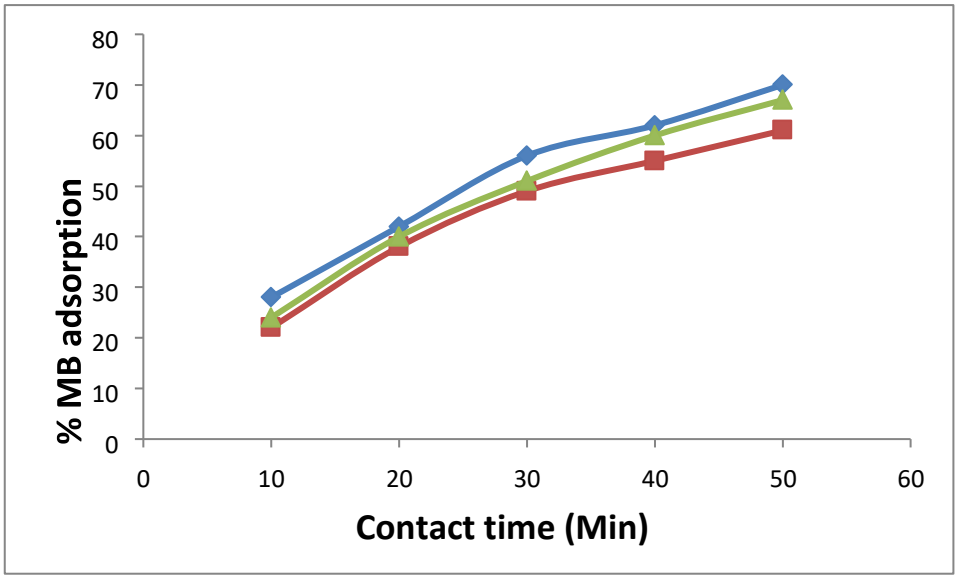

Figure 1: Effect of contact time on MB adsorption

Effect of methylene blue dye concentration

The amount of MB present in aqueous solutions has a significant impact on MB adsorption. The relationship between the adsorbent's adsorption capacity and the percentage of MB removed is depicted in Figure 2. In order to test the effect of MB concentration, 0.1 g of the biomass was mixed with 50 mL of MB solution in various Erlenmeyer flasks at various concentrations (50, 100, 150, 200, and 250 mg/L). A 120 rpm agitation rate was used to continuously stir the mixture in a temperature-controlled water bath. The difference between the initial and residual concentrations of MB in the liquid phase was used to calculate the amount that was adsorbed.

The adsorption of MB colour by the adsorbent at first high in totally enacted carbon and slowly diminishes than become steady when MB focus arrived at 250 mg/L. It could be because of the association between the colour and the dynamic destinations of the adsorbent. At higher focuses more MB colour are passed on un-adsorbed in arrangement because of the complete immersion of restricting destinations of the adsorbent. Expansion in the underlying convergence of MB gave a strong main impetus to defeat the mass exchange obstruction between the fluid and strong stages. The initial MB concentration of 50 mg/L produced the highest adsorption capacities.

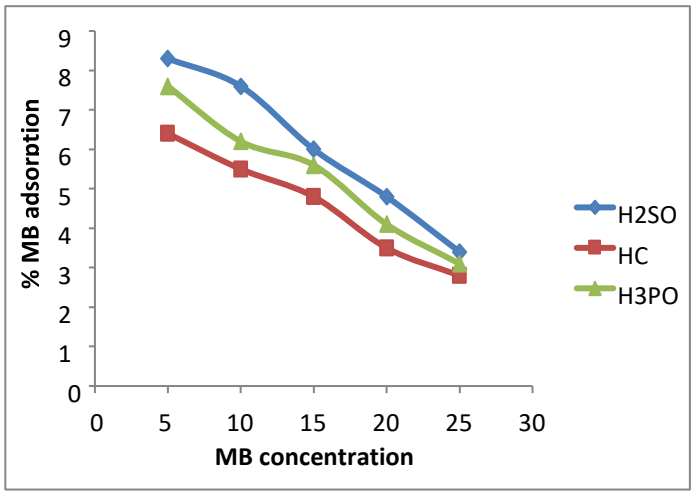

Figure 2: Effect of methylene blue concentration on adsorption

Effect of adsorbent dosage

The effect of adsorbent dose on adsorption capacity and adsorption efficiency of MB were studied on adsorbents derived from *Aegle Marmelos shell* by the activation of three different acids. Figure 3 illustrates that the adsorption efficiency augmented with the increase of the adsorbent amount, while the amount adsorbed decreases with increasing mass. This may probably due to the augmented surface area and number of active sites available for the fixation of methylene blue. The removal of MB by low cost adsorbent at different adsorbent doses (0.1 – 1g in 1000 mL) was studied. All process parameters like, contact time, agitation speed, and MB concentration was fixed. Figure-3 shows that, the adsorption capacity of MB dye increased rapidly with increase in the dose. The adsorption rate of adsorbent to remove MB dye increase with increase in biomass dose from 0.2 to 1 g/L of solution and after then it becomes stationary. The adsorption percentage was increased for sulphuric acid activated carbon from 40% to 93% while the adsorbent activated with hydrochloric acid adsorbed low amount of MB from 32% to 82%. Phosphoric acid activated adsorbent remove dye from aqueous solution from 32% to 88%, which is lower than H_2SO_4 but higher than HCl.

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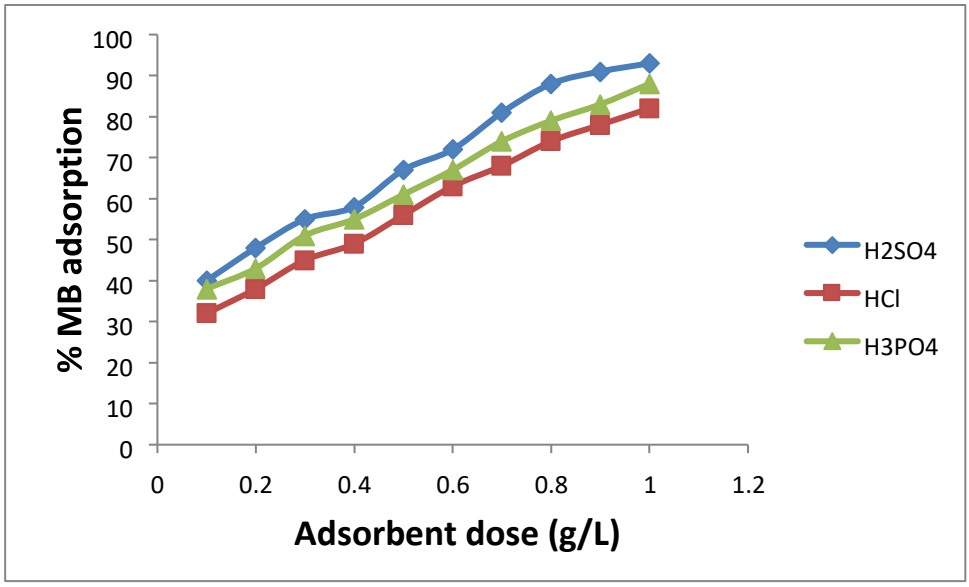
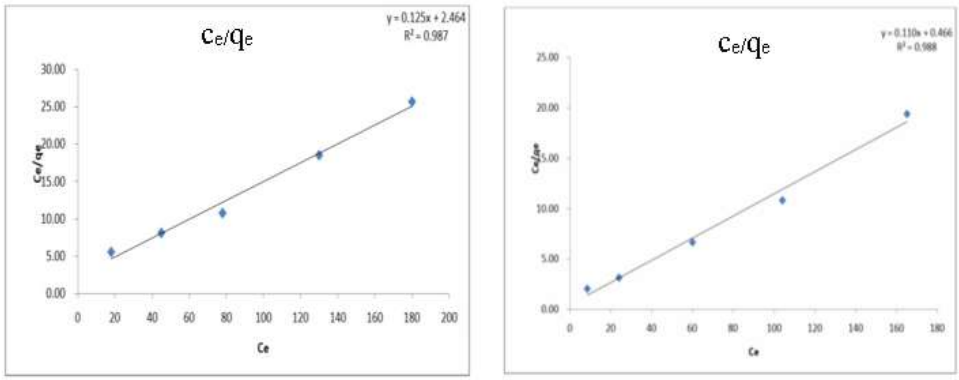


Figure 3: Effect of adsorbent doses on MB adsorption

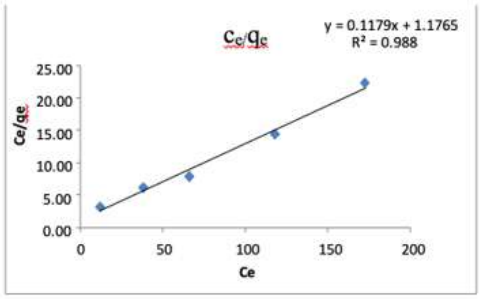
Adsorption equilibrium studies:

The equilibrium adsorption isotherm of Langmuir and Freundlich is used to analyze the experimental data. To identify the isotherm that represents the MB adsorption and comprehend the adsorption mechanism for various initial concentrations. The linear forms of the Langmuir and the Freundlich isotherms for the adsorption of methylene blue are compared in Figures 4 and 5. The Langmuir model, which has a higher correlation factor than the Freundlich model, is shown to be more applicable in Figure 4, suggesting the possibility of multilayer adsorption. The slope values (b) are also less than 1, indicating that the adsorption is favorable with an L-type isotherm (Shavandi et al., 2012).



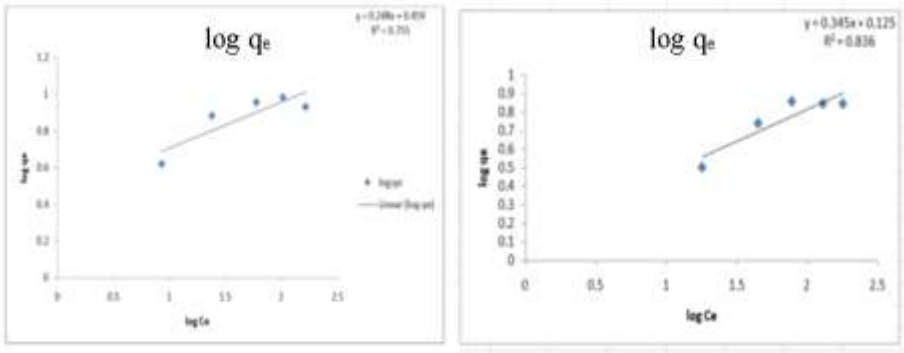
A. H_2SO_4 activated carbon

B. HCl activated carbon



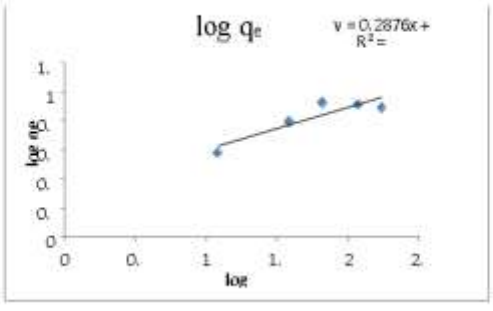
C. H_3PO_4 activated carbon

Figure 4. Langmuir isotherm plots for MB adsorption at different concentrations.



A. H2SO4 activated Carbon

B. HCl activated Carbon



C. H_3PO_4 activated carbon

Figure 5: Freundlich isotherm plots for MB adsorption at different concentrations.

Table 1: Isotherm parameters for the adsorption of Methylene blue on different activated carbon samples

Adsorbent		Langmuir Isotherm			Freundlich Isotherm		
AC	Q_m	b	Correlation Coefficient (R^2)	Separation Factor (R_L)	K_f	n	Correlation Coefficient(R^2)
H_2SO_4	9.09	0.23	0.988	0.041	0.459	4.03	0.755
HCl	8	0.05	0.987	0.054	0.345	2.89	0.836
H_3PO_4	8.5	0.09	0.988	0.059	0.314	3.48	0.821

The study of the adsorption kinetics is important to evaluate the mechanism and efficiency of effluents adsorption method (Senthilkumaar et al., 2005). Pseudo-first order and pseudo-second order kinetics models were used in this study to describe the MB dye's adsorption mechanism on activated carbon samples. The rate constant studies conducted using the pseudo-first-order and second-order models for various initial dye concentrations are presented in Table 2. The pseudo-second-order adsorption model's calculated equilibrium adsorption capacity and correlation coefficient are both high. Assuming that the adsorption of MB over as-prepared carbon materials is fitted by a pseudo-second order model, the calculated values match those of the practical experiments. In terms of the type of the activator, the pseudo-second order model rate constant (k_2) that was determined by the PSO model exhibited the following order: H_2SO_4 prevails over HCl. The higher adsorption rate of carbon materials activated with H_2SO_4 for MB removal was suggested by this trend. As a result, it is reasonable to assume that the pseudo-second-order kinetic model governs MB adsorption.

Table 2: Kinetic parameters for the adsorption of methylene blue on activated carbon samples.

	First-order kinetic model			Second-order kinetic model		
Q_e Experimental	k_1	Q_e Calculated	R^2	k_2	Q_e Calculated	R^2
25.8	0.018	22.9	0.992	0.001	28.6	0.990
25.8	0.018	23.4	0.997	0.0009	27	0.993
25.8	0.016	22.7	0.963	0.0008	30.3	0.999

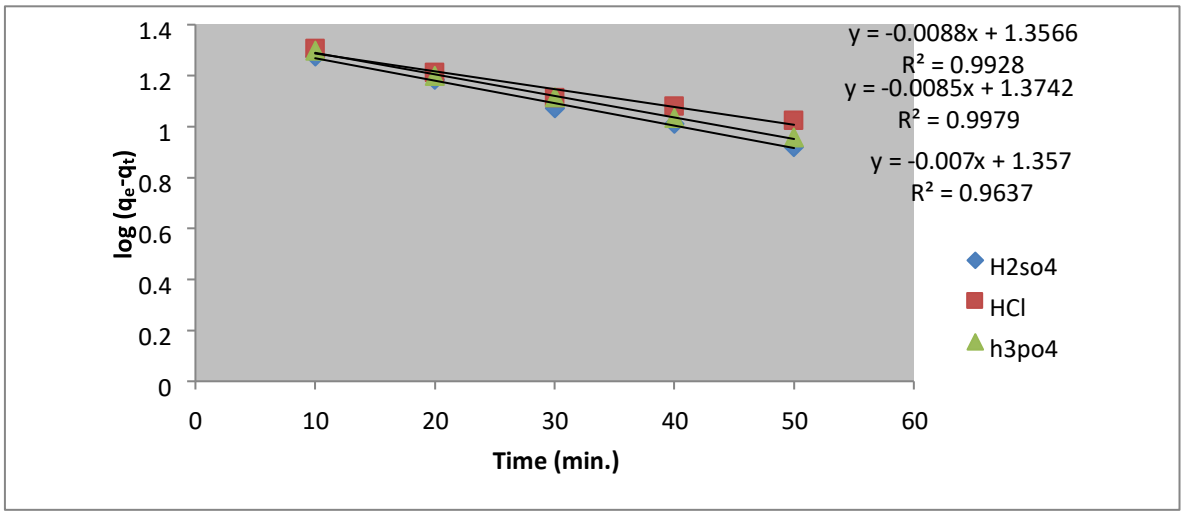


Figure 6: Experimental kinetic data and linear fitted curve with kinetic models for pseudo-first-order

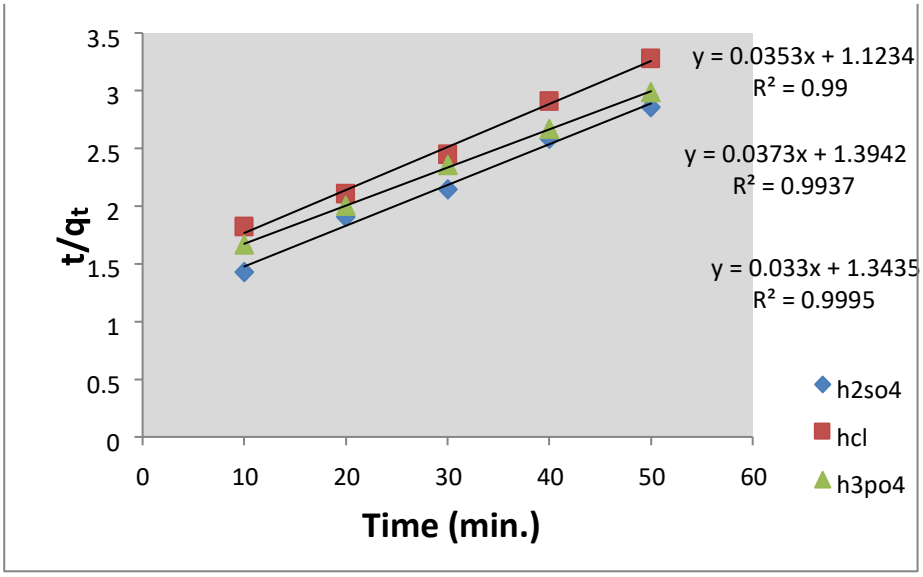


Figure 7: Experimental kinetic data and linear fitted curve with kinetic models for pseudo-second-order

In the current investigation, the Langmuir isotherm model provided the most accurate description of the equilibrium data after they were fitted to Langmuir isotherms. The pseudo-second-order kinetic model was found to be applicable to the adsorption process's kinetics. Similar study was conducted by Perera et al., (2018), they clearly reported that removal efficiency enhanced as the dose increased from 20-60 mg. Anand kumar and Mandal, (2009) prepared activated carbon from the abundantly available waste material of *Aegle marmelos* fruit shell using the phosphoric acid but they found maximum dye removal percentage at alkaline condition.

Conclusion

The creation of exceptionally effective permeable carbon materials got from *Aegle marmelos* organic products shell has been researched. Various activators (H_2SO_4, H_3PO_4, HCl.) are being used. Notwithstanding the enactment temperature and the substance specialist rate were advanced. As the solution contact time and adsorbent concentration increased, so did the percentage of dye removal, which decreased as the initial dye concentration increased. It was discovered that the presence of anionic surfactant increased sorption of the methylene blue, whereas the presence of cationic and non-ionic surfactants decreased it. The Langmuir isotherm model provided the most accurate description of the equilibrium data after they were fitted to Langmuir isotherms. The pseudo-second-order kinetic model was found to be applicable to the adsorption process's kinetics.

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