



Adsorption Studies of Methyl Violet Dye using Biosorbents

N Saravanan^{1*}, GRathika²

^{1*}Department of Chemistry, Nandha Engineering College, Erode 638052,
Tamil Nadu, India

²Department of Chemistry, PSG College of Arts and Science, Coimbatore 641014,
Tamil Nadu, India

Abstract : The batch adsorption experiments were carried out to remove methyl violet from aqueous solution using copper pod flower. In the present study, the use of low cost, abundantly available, highly efficient and eco-friendly biosorbent copper pod flower has been reported as an alternative to the current expensive methods of removing of methyl violet dye from aqueous solution. The objective of this study was to investigate the removal of methyl violet from synthetic wastewater by the biosorption on biosorbents. Effect of process parameters initial dye concentrations, adsorbent dosage, temperature (30, 40, 45, 50, 55 and 60°C), contact time and pH (2-12) were studied. Experimental tests were conducted in a batch process. The equilibrium data were analyzed using Freundlich, Langmuir isotherm, Tempkin and Dubinin – Radushkevich isotherm models. The equilibrium data were best represented by Freundlich isotherm model better than the Langmuir isotherm model. The dimensionless separation factor, R_L indicated that the biosorptions of the malachite green dye onto biosorbents were favourable. The pseudo-first order, pseudo-second order kinetic model, Elovich model and intraparticle diffusion model were used to examine the experimental data of different initial concentrations. From experimental data it was found that adsorption of methyl violet onto copper pod flower followed the pseudo-second order kinetic model. The adsorption process was found to be exothermic in nature. Surface morphology was also examined using Scanning Electron Microscopy. The characterization of biosorbent was investigated by scanning electron microscope and X-Ray diffraction data.

Keywords : Copper pod, Dye, Adsorption, Isotherm, Kinetic.

1. Introduction

Water pollution has become an environmental problem worldwide as well as local. The most concerned environmental pollution is wastewater pollution^[1]. Developing countries in Asia are threatened by environmental pollution due to the lack of waste treatment facilities. Most wastewater treatment technologies are known as being costly and not affordable by the municipalities and the small scale polluting industries^[2]. Textile industries discharged a large quantity of highly coloured wastewater effluent which are released into nearby land or rivers without any treatment^[3]. Thus the removal of colour from effluents is one of the major environmental problems. Decolourisation of wastewater has become one of the major issues in wastewater

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pollution^[4]. This is because many industries used dyes to colour their products, such as textiles, paper, plastics, leather, rubber, cosmetics, food and mineral processing industries. Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries^[5]. There are more than 100,000 commercially available dyes with over 7x10⁵ tonnes of dyes produced annually. Various physicochemical and biological techniques can be employed to remove dyes from wastewaters^[6]. They include the membrane filtration, coagulation, flocculation, adsorption, ion exchange, advanced oxidation, flotation, chemical reduction and biological treatment^[7]. In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances.

2. Materials and methods

2.1 Preparation of adsorbents

The present studies Copper Pod flowers were used as biosorbent for the removal methyl violet dye from aqueous solution. They were collected from in around PSG College of Arts and Science, Coimbatore District, Tamilnadu, India which were available in abundant.

The copper pod flowers were washed thoroughly with ordinary tap water to remove any dust and twice with distilled water. The washed materials were dried in sun light to evaporate the moisture present in it. The dried material was ground to fine powder and then sieved with a particle size of 53 μ m. The sieved adsorbent sample prepared was kept in an airtight container and used for further adsorption studies.

2.2 Preparation of Adsorbate

A stock solution of 1000mg/L was prepared by dissolving 1 gm of methyl violet dye in a 1litre of distilled water. All working solutions used in tests were prepared by diluting the stock solution with distilled water to get the appropriate concentration. The dye concentration was determined at characteristic wavelength ($\lambda_{\text{max}} = 590\text{nm}$) by using UV/visible spectrometer (Elico, SL-171).

2.3 Adsorption studies

Adsorption experiments were performed by the batch technique to obtain rate and equilibrium data. Batch adsorption experiments were carried out to investigate the effect of initial dye concentration, contact time, pH, carbon dosage and temperature on the adsorption of methyl violet on copper pod flower. The experiments were carried out in 150ml conical flasks by mixing a pre-weighed amount of adsorbent with 50ml of methyl violet dye solution. The adsorbent dosages were checked from 0.1 – 1g/L. The isotherm study was carried out at different temperature from 30 to 60°C with the initial dye concentrations of 10 to 50mg/l. The kinetic study was done by varying time from 0 to 100min. The effect of pH was observed by studying the adsorption of dye over a pH range of 2 – 12. The pH of the dye solution was adjusted with 0.1N HCl or 0.1N NaOH solution by using a pH meter (EUTECH Instrument, pH 510). The equilibrium adsorption capacity was calculated using the following equation,

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where, q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations(mg/L) of dye solution. V is the volume of dye solution (mL) and M is the weight of adsorbent (g).

3. Results and Discussion

3.1 Effect of contact time and initial dye concentration

The results obtained indicate that the percentage of dye removal increased with contact time rapidly and became constant when equilibrium was attained^[8]. The percentage of dye removal increased with increase in initial dye concentration. It was found that the percentage of dye removal dependent on the concentration of the dye.

3.2 Effect of adsorbent dosage

The result suggests that increased adsorbent dosages increased the percentage removal of dye^[9]. Higher dosage of adsorbent increased the adsorption due to more surface area and functional groups are available on the adsorbent.

3.3 Effect of pH

The percentage of dye removal was increased upto pH 7. The maximum percentage of dye removal was obtained at pH 7 for all the concentration of the dye solution. At low pH, the adsorbent surface becomes negatively charged and favours uptake of cationic dyes due to increased electrostatic forces of attraction. At high pH, the adsorbent surface becomes positively charged and high concentration of H⁺ ions which compete with cationic methyl violet dye causing decrease in dye uptake^[10].

3.4 Effect of Temperature

The adsorption capacities of methyl violet dye decreased with the incremental temperature from 30 to 60°C for 40mg/lit. It is because higher temperature may decrease the adsorptive forces between the dye molecules and active sites on the adsorbent^[11]. The maximum percentage removal of dye was obtained at 30°C. Therefore, adsorption process is exothermic in nature.

3.5 Analysis of adsorption Kinetics

Adsorption is time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the dyes in wastewater. Various kinetic models have been used to describe the adsorption process. The pseudo first order and pseudo second order kinetic models are the most widely used models for the adsorption of solutes from a liquid solution.

3.5.1 Pseudo-first order equation

The pseudo first-order rate expression of Lagergren is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

Where, q_e is the amount of dye removed at equilibrium (mg/g)

q_t is the amount of dye removed at time t (mg/g)

k_1 is the pseudo- first order rate constant (min⁻¹)

The values of k_1 and calculated q_e were determined from the slope and intercept of the linear plot of $\log(q_e - q_t)$ versus time (t) gives a linear relationship and is shown in figure.1. The pseudo first order rate constant (k_1), correlation coefficients (R^2), experimental q_e values and calculated q_e values are presented in table.1. Values of k_1 for removal of methyl violet dye by copper pod flower were 0.0115, 0.0161, 0.0253, 0.0276 and 0.0368. Values of correlation coefficients (R^2) together with the large deviation between calculated q_e values and the experimental q_e values indicated that the adsorption of methyl violet dye on copper pod flower not obeys the pseudo first order reaction^[12].

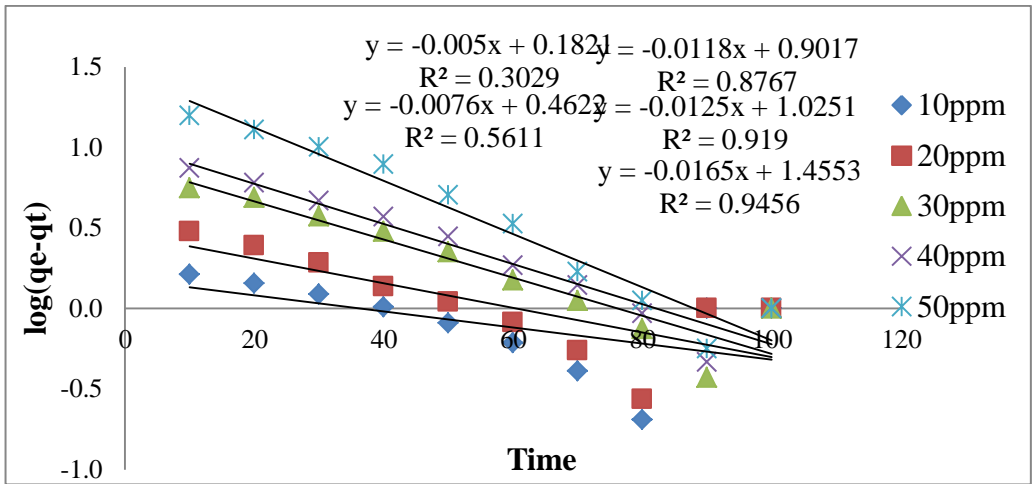


Figure 1: Pseudo-first order kinetics for adsorption of methyl violet onto copper pod flower.

3.5.2 Pseudo-second order equation

The pseudo second-order rate expression of Lagergren is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

Where, q_e is the amount of dye removed at equilibrium (mg/g)

q_t is the amount of dye removed at time t (mg/g)

k_2 is the pseudo- second order rate constant (min^{-1})

The figure.2 shows various initial dye concentration of pseudo second order kinetic model. k_2 and q_e values can be determined from the slope and intercept of the plot of $\frac{t}{q_t}$ versus t. The results are given in in table.1. From the table 1, it was noticed that R^2 values for the pseudo second order kinetic model is higher ($R^2 = 0.983 - 0.999$) than that of the pseudo first order kinetic model ($R^2 = 0.510 - 0.853$) for all initial dye concentrations. The calculated q_e values obtained from the pseudo second order kinetics model good agreement with the experimental q_e values^[13]. Values of k_2 for removal of methyl violet dye by copper pod flower were 0.1683, 0.0131, 0.0066, 0.0450 and 0.0490. This shows that the adsorption of methyl violet dye on copper pod flower is well suitable for the pseudo second order kinetic model with compared to the pseudo first order kinetic model. It also suggests that chemisorption process could be the rate limiting step in the adsorption process.

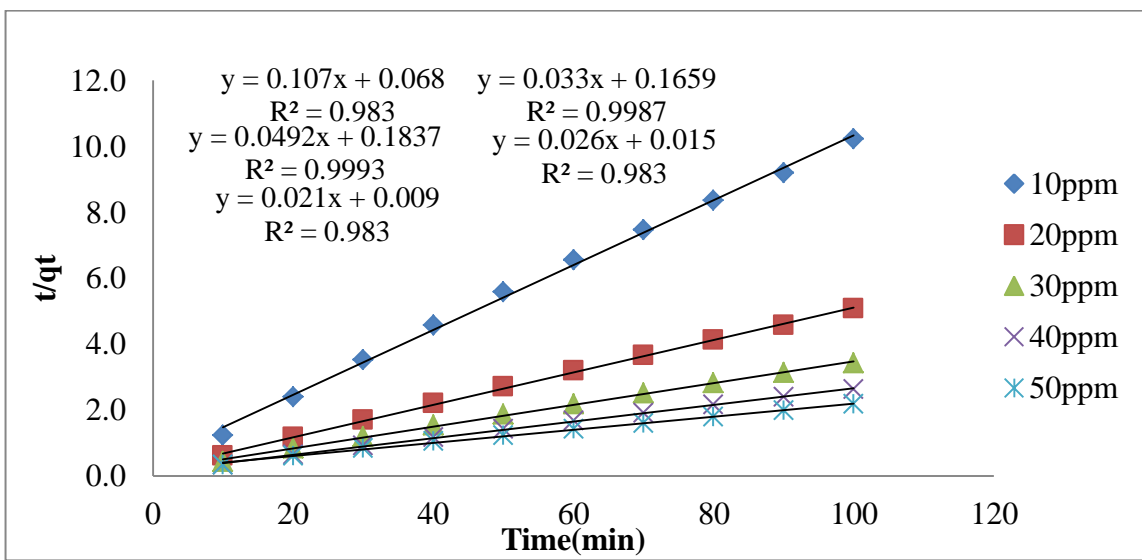


Figure 2: Pseudo- second order Kinetics for the adsorption of methyl violet onto copper pod flower.

Table.1: Results of kinetic plots for the adsorption of methyl violet onto copper pod flower.

Concentration (mg/L)	10	20	30	40	50
Pseudo-first-order					
q_{exp} (ppm)	9.80	19.73	29.25	38.14	46.07
q_{ecal} (ppm)	1.52	2.89	7.96	10.59	28.51
k_1 (ppm)	0.0115	0.0161	0.0253	0.0276	0.0368
R^2	0.302	0.561	0.876	0.919	0.949
Pseudo-second-order					
q_{ecal} (ppm)	9.34	20.40	30.30	38.46	47.61
k_2 (ppm)	0.1683	0.0131	0.0066	0.0450	0.0490
R^2	0.983	0.999	0.998	0.983	0.983
Intraparticle					
C	7.215	15.29	20.81	27.33	22.74
K_d (mg/g.min)	0.259	0.462	0.860	1.108	2.459
R^2	0.983	0.992	0.993	0.993	0.981
Elovich model					
β	4.76	2.98	1.59	1.24	0.56
R^2	0.901	0.954	0.963	0.953	0.935

3.5.3 Intra particle diffusion studies

The Intraparticle diffusion model is used for confirming the mechanism of the adsorption process. Intraparticle diffusion (k_d) is given by weber morris and is expressed as follows

$$q_t = k_d t^{1/2} \tag{4}$$

Where, q_t is the amount adsorbed (mgg^{-1}) at time t (min).

k_d is the rate constant of intraparticle diffusion ($\text{mgg}^{-1}\text{min}^{1/2}$).

The plot of amount adsorbed (q_t) versus time gives straight line and is shown in figure.3. The rate constant of intraparticle diffusion (k_d) can be determined from slope of the straight line and the values are listed in table.1. The linear portion of the plot at each concentration did not pass through the origin suggesting that intraparticle diffusion was not the only rate controlling step^[14]. The high correlation coefficient (R^2) values ($R^2 = 0.981 - 0.993$) obtained at each concentration indicated that the pore diffusion plays a significant role for the adsorption of methyl violet dye onto the activated carbon prepared from copper pod flower.

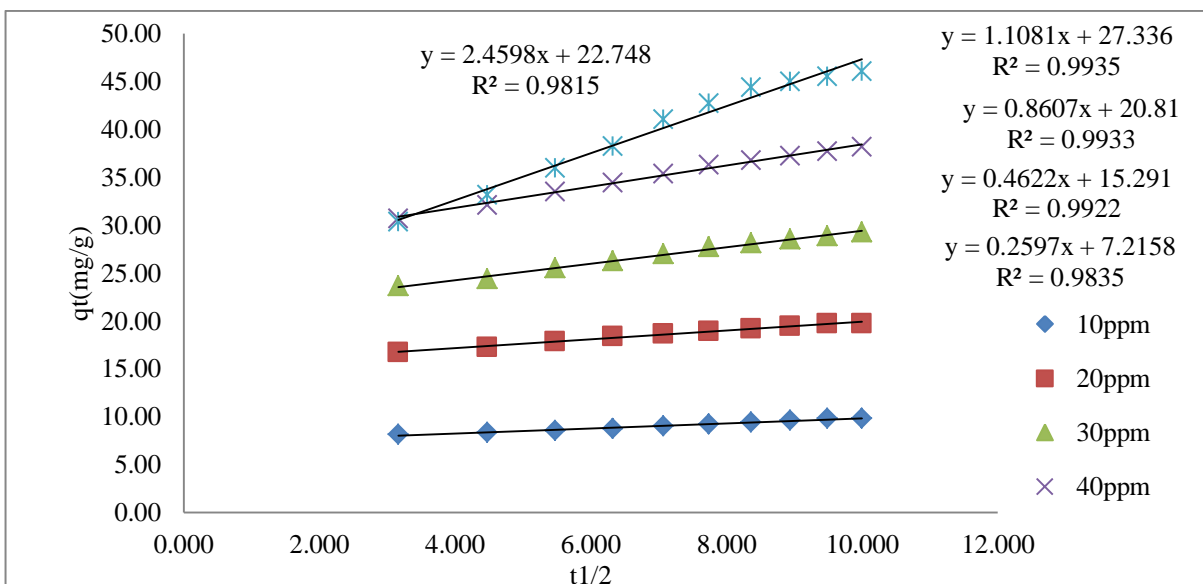


Figure 3: Intra particle diffusion for the adsorption of methyl violet onto copper pod flower.

3.5.3 Elovich Model

Elovich model is one of important model for describing adsorption and is expressed as follows

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (5)$$

Where, α is the initial adsorption rate constant (mg/g min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

Integrating this equation for the boundary conditions, expressed as follows

$$q_t = 1/\beta [\ln(\alpha\beta)] + 1/\beta \ln t \quad (6)$$

α and β values can be calculated from the slope and intercept of plots q_t Vs $\ln t$ and is shown in Figure 4. β and R^2 values were presented in table.1. It has been suggested that an increase in α value and/or decrease in β value would increase the rate of the adsorption process^[15]. The plot is linear with good correlation coefficient (0.901 to 0.963).

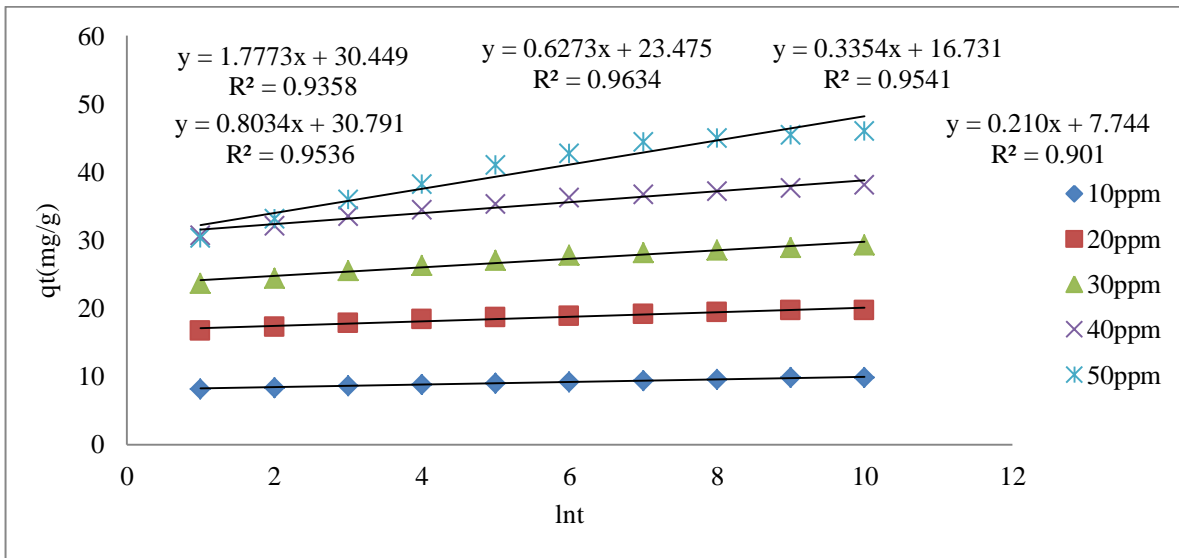


Figure 4:Elovich model for the adsorption of methyl violet onto prepared onto copper pod flower.

3.6 Adsorption isotherm

The adsorption process is used to remove colour and other soluble organic pollutants from effluent^[16]. Adsorption isotherms are known as equilibrium data, are the fundamental requirements for the design of adsorption systems. The adsorption isotherm describes the mechanism of the adsorption process between the adsorbate and the adsorb^[17]. The Langmuir and Freundlich isotherm were analysed to study the adsorption isotherm of dye.

3.6.1 Langmuir isotherm

The langmuir isotherm equation is expressed as follows.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

Where, q_e is the amount of dye adsorbed at equilibrium (mgg^{-1})

C_e is the concentration of dye solution at equilibrium (mgL^{-1})

Q_0 is Langmuir constant related to adsorption capacity (mgg^{-1})

b is Langmuir constant related to rate of adsorption(Lmg^{-1})

Values of Q_0 and b were calculated respectively from the slope and the intercept of the plot of $\frac{C_e}{q_e}$ versus C_e gives a straight line and is shown in figure.5.Langmuir parameters and correlation coefficient (R^2) values were summarized in table.2.

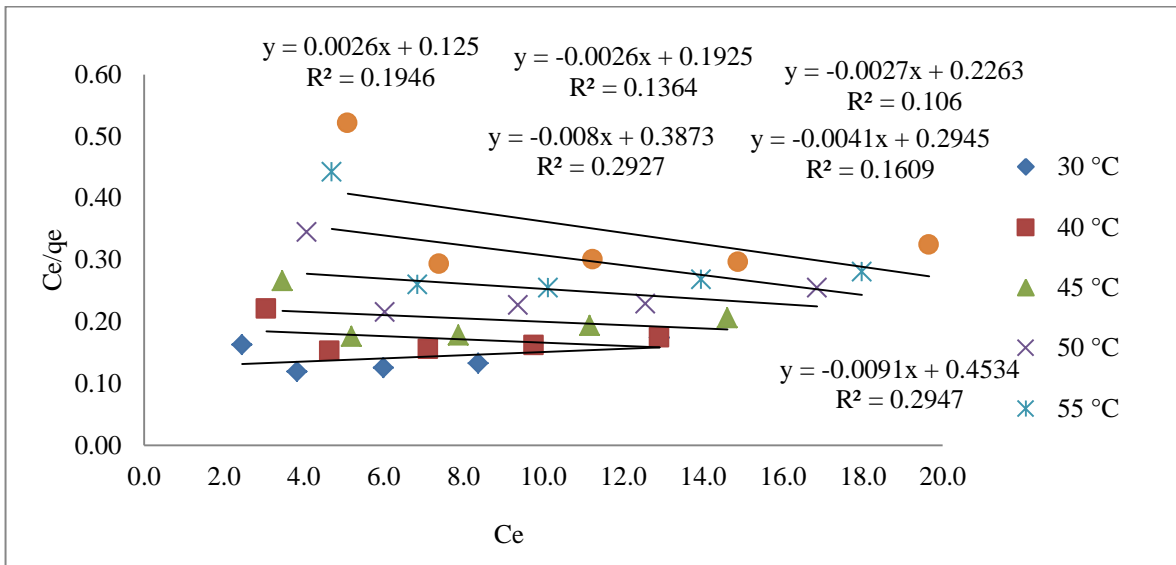


Figure 5: Langmuir isotherm for the adsorption of methyl violet onto copper pod flower.

Table. 2: Results of various isotherm parameters

Temp.(°C)	30°C	40°C	45°C	50°C	55°C	60°C
Langmuir Isotherm Constants						
b (L/mg)	0.0160	0.0104	0.0088	0.0136	0.0206	0.0198
Q_0 (mg/g)	500	500	500	250	125	111
R^2	0.194	0.136	0.106	0.160	0.292	0.294
Freundlich Isotherm Constants						
k_f (mg/L)	7.798	4.570	3.837	2.766	1.811	1.479
n	1.0582	0.8857	0.8873	0.8554	0.7830	0.7728
R^2	0.933	0.960	0.949	0.943	0.939	0.933
Tempkin Isotherm Constants						
B	36.25	41.29	39.32	15.01	9.44	37.18
A	0.1128	0.2876	0.3353	0.1352	0.1618	0.4793
R^2	0.994	0.996	0.997	0.873	0.775	0.996
Dubinin-Radushkevich isotherm						
Xm (mg/g)	73.05	73.71	71.11	67.57	67.44	64.34
E (KJ/mol)	31.31	48.79	40.16	39.92	31.31	26.53
R^2	0.989	0.981	0.986	0.986	0.991	0.990

From table.2.the Langmuir maximum adsorption capacity Q_0 are 500, 500, 500, 250, 125 and 111(mg/g) at 30,40,45,50,55 and 60°C respectively.The obtained results from Langmuir isotherm indicate the exothermic nature process involved in the system. Table.2. clearly showed that lack of fit the data for Langmuir isotherm model^[18].

The essential characteristics of Langmuir isotherm equation can be expressed in terms of dimensionless separation factor, R_L , which is defined by the following equation^[19].

$$R_L = \frac{1}{1 + bc_0}$$

Where C_0 is the initial concentration of dye solution (mgL^{-1}) and b is the Langmuir constant. The value of R_L indicates that the type of the isotherm to be either linear ($R_L = 1$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), or irreversible ($R_L = 0$). R_L values for the present experiment data fall between 0 and 1, which clearly indicates the adsorption of methyl violet dye on copper pod flower was favourable.

3.6.2 Freundlich Isotherm

The Freundlich isotherm equation was given by

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log C_e \quad (8)$$

Where, q_e is the amount of dye adsorbed (mg g^{-1})

C_e is the concentration of dye solution at equilibrium (mgL^{-1})

k_f is Freundlich constant related to the adsorption capacity of adsorbent

n is Freundlich constant related to the adsorption intensity

k_f and n values can be calculated from the slope of the straight line and is shown in figure.6. The Freundlich parameters and the results are represented in table.2.

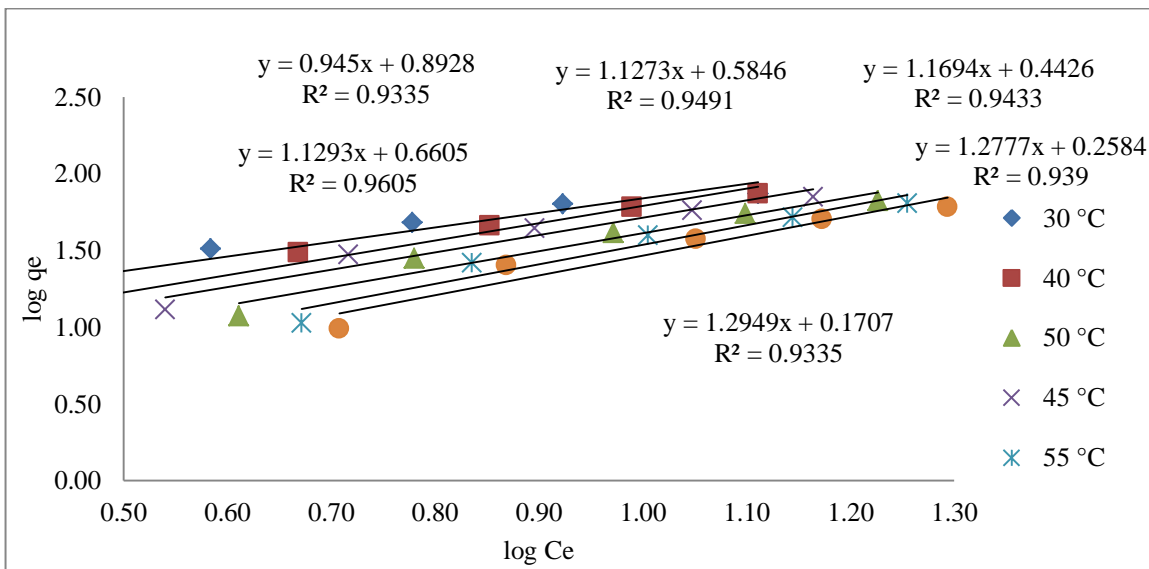


Figure 6: Freundlich isotherm for the adsorption of methyl violet onto copper pod flower.

A value for n ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as its gets value closer to zero^[20]. Values of n for removal of dye by copper pod flower were 1.0582, 0.8857, 0.8873, 0.8554, 0.7830 and 0.7728 respectively. The n values are between 0 and 1 representing beneficial adsorption. A value of n less than one indicates that better adsorption mechanism and formation of relatively stronger bond between dye molecules and adsorbents. This shows that copper pod flower are better adsorbent for the methyl violet dye. Values of K_f for removal of dye by copper pod flower were 7.798, 4.570, 3.837, 2.766, 1.811 and 1.479 respectively. The value of K_f also indicates that adsorption capacity of the adsorbent. The higher the K_f values greater is the adsorption capacity of an adsorbent. Results shows that the experimental data was better described by the Freundlich isotherm model compared to the Langmuir isotherm model. The value of correlation co-efficient (R^2) is regarded as a measure of the goodness-of-fit of experimental data. The values of correlation co-efficient (R^2) indicated that the adsorption process conforms to the Freundlich isotherm model. This shows that the experimental data was better explained by the Freundlich isotherm model ($R^2 = 0.933$ to 0.960) compared to the Langmuir isotherm model. This indicates that the adsorption of methyl violet dye on copper pod flower takes place as monolayer adsorption on the adsorbent surface, homogenous in adsorption affinity^[21].

3.6.3 Tempkin isotherm

Tempkin isotherm assumes that the heat of adsorption of all the molecules and the adsorbent-adsorbate interaction on adsorption^[22]. The linear form of Tempkin isotherm equation is given as follows

$$q_e = B (\ln A + \ln C_e) \tag{9}$$

Where, B is the Tempkin constant related to heat of adsorption

A is the equilibrium binding constant (mg/l)

The values of the Tempkin constants A and B can be calculated from the intercept and slope of the linear plot of $\ln C_e$ versus q_e and is shown in Figure.7. Values of B were in the range of 9.44 – 41.29, while values of A in the range of 0.1128 – 0.4793. The correlation coefficients (R^2) values are listed in table.2. The result shows that Tempkin adsorption isotherm was not applicable to explain the methyl violet adsorption onto copper pod flower.

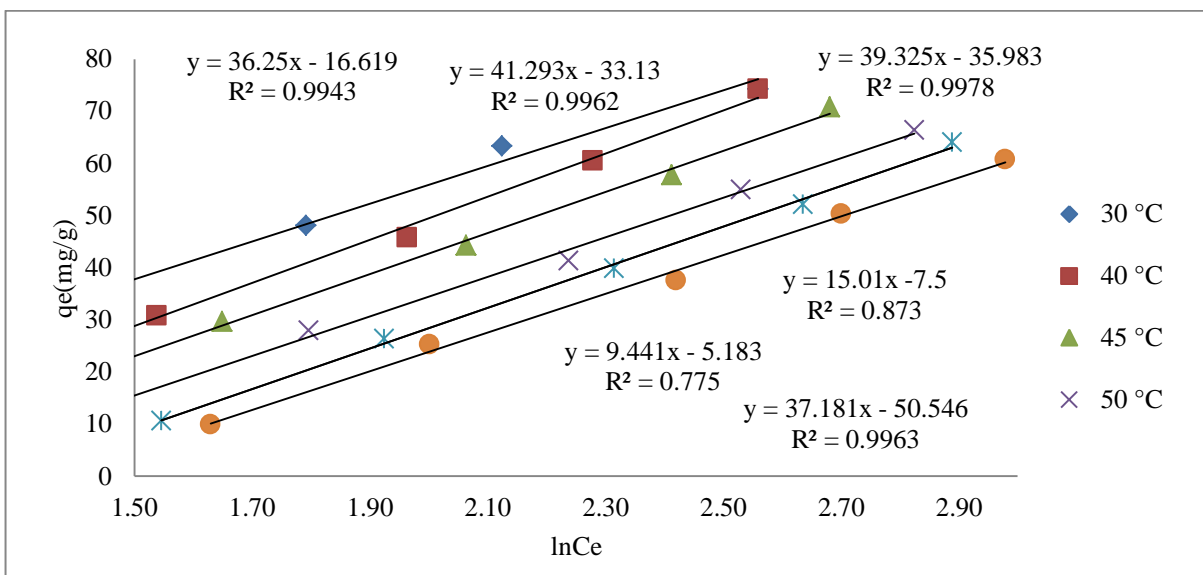


Figure 7:Tempkin isotherm for the adsorption of methyl violet onto copper pod flower.

3.6.4 Dubinin-Radushkevich isotherm (D – R EQUATION)

The linear form of the Dubinin-Radushkevich isotherm equation can be expressed as follows

$$\ln q_e = \ln X_m - \beta E^2 \tag{10}$$

Where, X_m is the theoretical saturation capacity (mg/g), β is a constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and E^2 is the Polanyi potential. The values of E , X_m and β can be calculated from the slope and intercept of the plot of E^2 versus $\ln q_e$ gives a straight line. The correlation coefficients (R^2), E , X_m and β values are listed in table.2.

The mean free energy of adsorption E is determined from β using the following equation

$$E = 1/ (2\beta)^{1/2} \tag{11}$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorptions. If the energy of activation is, $<8 \text{ kJ mol}^{-1}$, the adsorption is physisorption. If the energy of activation is $8 \text{ to } 16 \text{ kJ mol}^{-1}$, the adsorption is chemisorptions^[23, 24]. The activation energy of adsorption decreases with increase of temperature from 30 to 60 °C. E is $> 11 \text{ kJ mol}^{-1}$ indicates the adsorption of methyl violet green onto copper pod flower is chemisorption in nature.

4. Conclusion

The adsorption of methyl violet dye from aqueous solution using copper pod flower as the low-cost biosorbent was investigated in batch process. The adsorption process was initial metal ion concentration, adsorbent dosage, contact time and pH dependent. The equilibrium data was best represented by Freundlich isotherm model. From the kinetic data, it was found that adsorption process follows pseudo second order kinetic model. The results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate limiting step. R_L values indicate favorable adsorption process. From the experimental results it was observed that the optimum pH was found to be pH = 7. Kinetic and equilibrium data revealed that dye removal by the studied adsorbents proceeded through physical adsorption and chemical adsorption mechanisms. From the results of the study it can be concluded that copper pod flower could be used effectively for the removal of methyl violet aqueous solutions.

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