Adsorption Studies of Malachite Green Dye Using Biosorbents

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Abstract

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 malachite green dye from aqueous solution. The objective of this study was to investigate the removal of malachite green from synthetic wastewater by the biosorption on biosorbents. Batch adsorption studies were conducted to examine the effects of initial dye concentrations, adsorbent dosage, temperature (30, 40, 45, 50, 55 and 60^oC), contact time and pH (2-12). Experimental tests were conducted in a batch process. The experimental isotherms data were analyzed using Freundlich, Langmuir, Tempkin and Dubinin - Radushkevich isotherm models. It was found that Freundlich isotherm model fit the isotherm data better than the Langmuir isotherm. 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 and intraparticle diffusion model were used to examine the experimental data of different initial concentrations. The adsorption kinetics of malachite green could be described by 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.

Key words: Copper pod, Dye, Adsorption, Isotherm, Kinetic.

Introduction

Water pollution has become an environmental problem worldwide as well as local. The most concerned environmental pollution is wastewater pollution [1]. Wastewater pollution comes from the industrial effluent and also from the domestic sewage. Water pollution is the contamination of water bodies such as lakes, rivers, oceans, aquifers and groundwater [2]. Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities [3]. Decolourisation of wastewater has become one of the major issues in wastewater pollution. This is because many industries used dyes to colour their products, such as textiles, paper, plastics, leather, rubber, cosmetics, food and mineral processing industries. These dyes are invariably left in the industrial wastes [4]. Since they have a synthetic origin and complex aromatic molecular structures, which make them inert and difficult to biodegrade when discharged into waste streams people overlook their undesirable nature. The presence of very low concentrations of dyes in effluent is highly visible and undesirable [5]. Malachite green is one of the most toxic dyes must be removed from wastewater due to its carcinogenic and mutagenic effects on life organisms. Several processes have been applied for the treatment of dyes from wastewater such as physical, biological and chemical process [6]. However, these methods are not widely used due to their high cost and economic disadvantage. Adsorption processes have been tried in many researches for the removal of dyes from wastewater. Activated carbon has been widely used as adsorbent material due to the large surface area. The most common adsorbent materials are: alumina silica, metal hydroxides and activated carbon [7]. As proved by many researchers, removal of dyes by activated carbon is economically favorable and technically easier.

Materials and Methods

Preparation of adsorbents

The present studies Copper Pod flowers were used as biosorbent for the removal Malachite green 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 μm. The sieved adsorbent sample prepared was kept in an airtight container and used for further adsorption studies.

Preparation of adsorbate

A stock solution of 1000mg/L was prepared by dissolving 1 gm of Malachite green 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 (λ_{max} = 617nm) by using UV/visible spectrometer (Elico, SL-171).

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 Malachite green on copper pod flower. The experiments were carried out in 150ml conical flasks by mixing a pre-weighed amount of adsorbent with 50ml of Malachite green 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^{o}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).

Results and discussion

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.

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.

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 malachite green dye causing decrease in dye uptake [10].

Effect of Temperature

The adsorption capacities of malachite green dye decreased with the incremental temperature from 30 to 60^{o}C for 40mgs/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^{o}C. Therefore, adsorption process is exothermic in nature.

Analysis of adsorption Kinetics

The study of adsorption kinetics is an important characteristic in describing the efficiency of adsorption process [12]. 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.

Pseudo-first order equation

The pseudo- first order equation of lagergen is expressed as follows.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

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 malachite green dye by copper pod flower were 0.0184, 0.0230, 0.0253, 0.0299 and 0.0276.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 malachite green dye on copper pod flower not obeys the pseudo first order reaction [13].

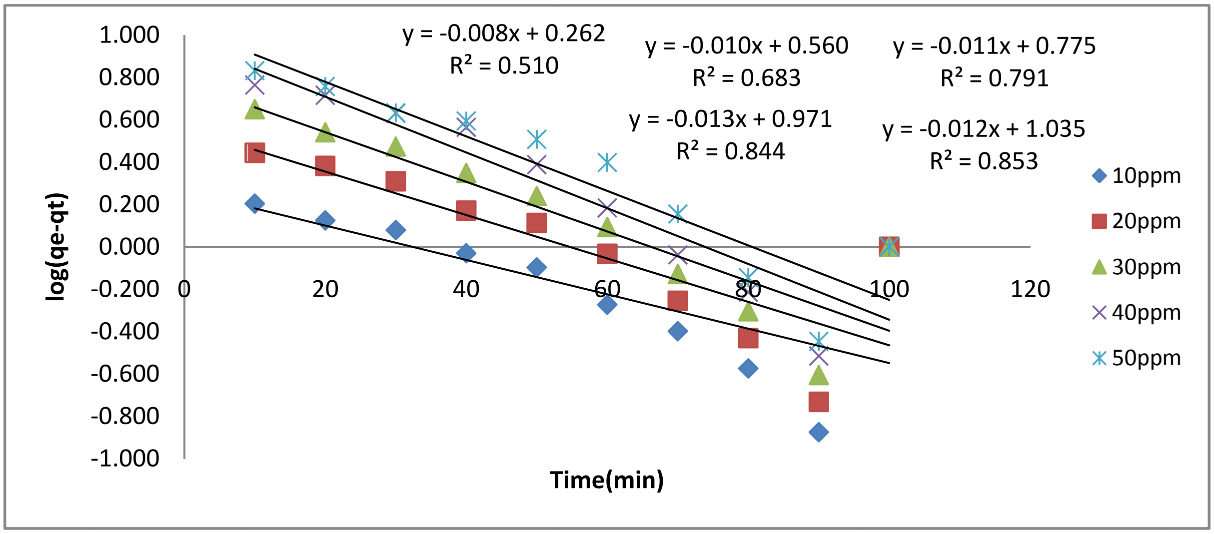

Figure 1.Pseudo-first order kinetics for adsorption of malachite green onto prepared activated carbon at 30°C

Pseudo-second order equation

The pseudo second order equation is expressed as follows.

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

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_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 = 0.997 – 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 [14]. Values of k_2 for removal of malachite green dye by copper pod flower were 0.1683, 0.0131, 0.0086, 0.0450 and 0.0490.This shows that the adsorption of malachite green 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.

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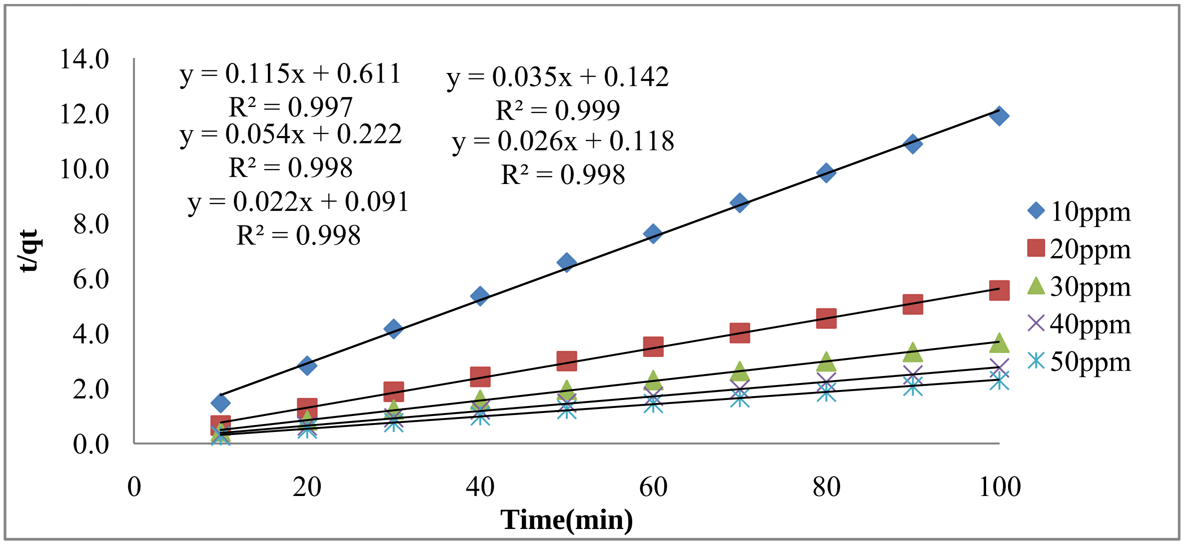

Figure 2. Pseudo- second order Kinetics for the adsorption of malachite green onto prepared activated carbon at 30°C

Table 1. Pseudo first and pseudo second order kinetic parameters for different initial dye concentration

Initial Conc.(ppm)	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
	q_{eexp} (ppm)	q_{ecal} (ppm)	k_1 (ppm)	R^2	q_{eexp} (ppm)	q_{ecal} (ppm)	k_2 (ppm)	R^2
10	8.40	1.82	0.0184	0.510	8.40	9.34	0.1683	0.997
20	17.96	3.63	0.0230	0.683	17.96	18.51	0.0131	0.998
30	27.27	5.95	0.0253	0.791	27.27	28.57	0.0086	0.999
40	36.34	9.35	0.0299	0.844	36.34	38.46	0.0450	0.988
50	43.57	10.83	0.0276	0.853	43.57	47.61	0.0490	0.998

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

$$q_t = k_d t^{1/2} \qquad (3)$$

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

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

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. 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 [15].The high correlation coefficient (R^2) values (R^2 = 0.979 – 0.992) obtained at each concentration indicated that the pore diffusion plays a significant role for the adsorption of malachite green dye onto the activated carbon prepared from copper pod flower.

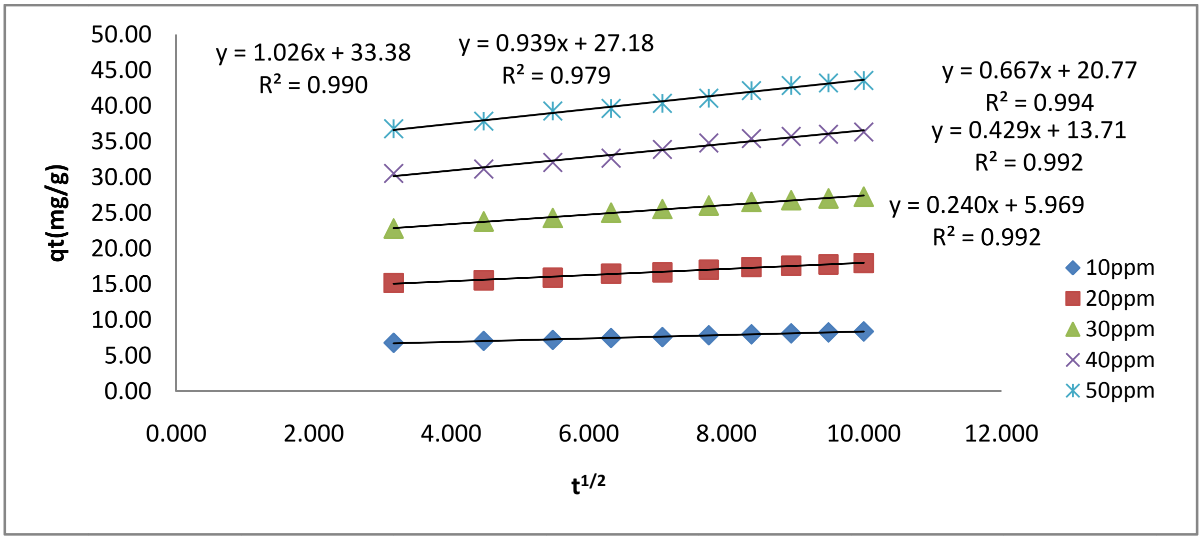

Figure 3. Intra particle diffusion for the adsorption of malachite green onto prepared activated carbon at 30°C

Elovich Model

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

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (4)$$

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

$$q_t = 1/\beta[\ln(\alpha\beta)] + 1/\beta \ln t \quad (5)$$

α and β values can be calculated from the slope and intercept of plots qt Vs lnt and is shown in Figure 4. It has been suggested that an increase in α value and/or decrease in β value would increase the rate of the adsorption process [16]. The plot is linear with good correlation coefficient (0.901 to 0.979).

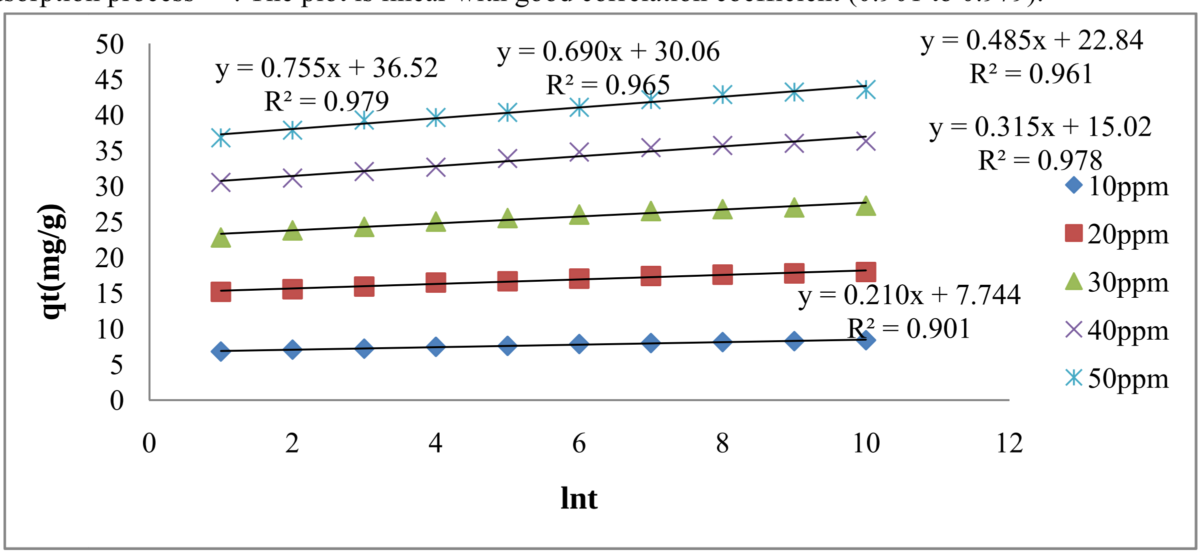

Figure 4. Elovich model for the adsorption of malachite green onto prepared activated carbon at 30°C

Adsorption isotherm

The adsorption isotherm describes the mechanism of the adsorption process between the adsorbate and the adsorb. The Langmuir and Freundlich isotherm were analysed to study the adsorption isotherm of dye.

Langmuir isotherm

The langmuir isotherm equation is expressed as follows.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (6)$$

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.

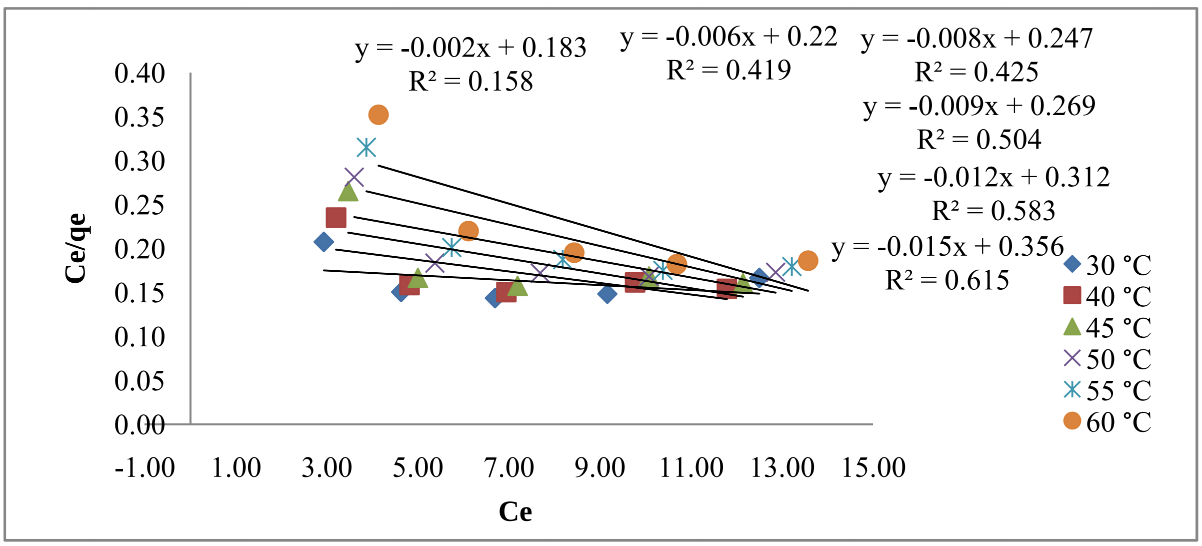

Figure 5. Langmuir isotherm for the adsorption of malachite green onto prepared activated carbon.

Table 2. Langmuir isotherm parameters

Temp.(D_c)	Langmuir Constants		
	R^2	Q_0(mg/g)	b. (L/mg)
30	0.158	500	0.0109
40	0.419	166	0.0272
45	0.425	125	0.0323
50	0.504	111	0.0334
55	0.583	83	0.0384
60	0.615	66	0.0421

From table 2. the Langmuir maximum adsorption capacity Q_0 are 500, 166, 125, 111, 83 and 66(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 4. clearly showed that lack of fit the data for Langmuir isotherm model [17].

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.

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

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 malachite green dye on activated carbon was favourable.

Freundlich Isotherm

The Freundlich isotherm equation was given by

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log C_e \qquad (7)$$

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.3.

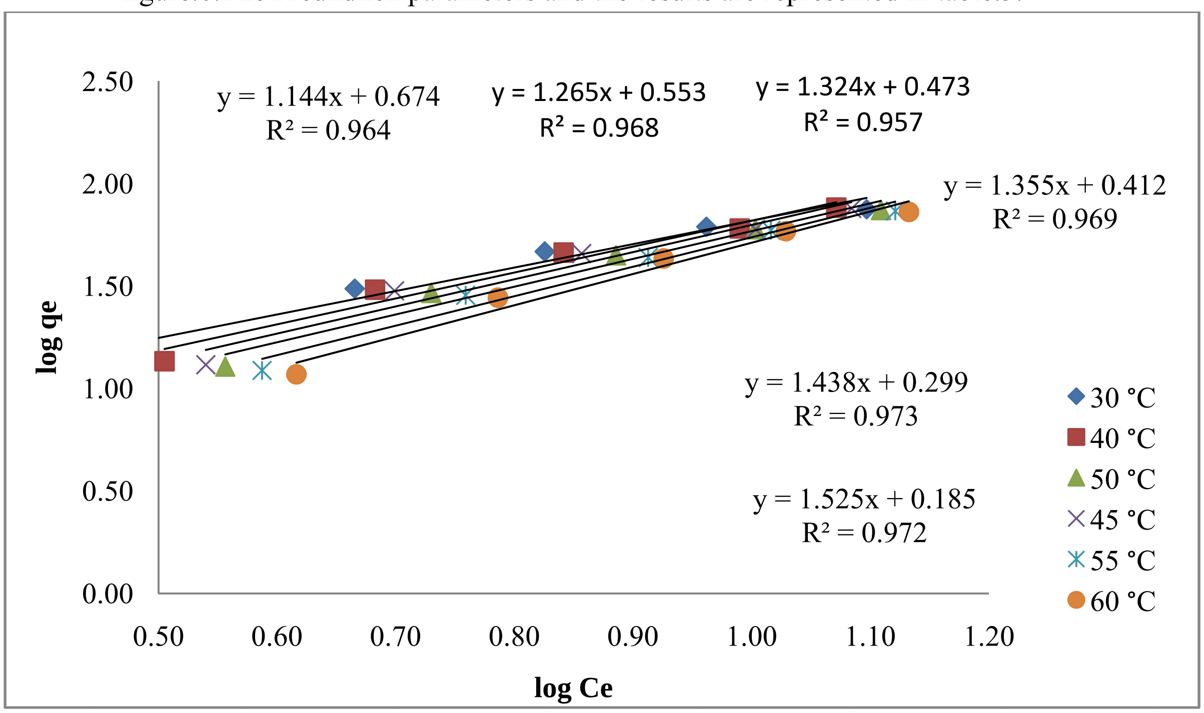

Figure 6. Freundlich isotherm for the adsorption of malachite green onto prepared activated carbon.

Table 3. Freundlich isotherm parameters

Temp.(0 ^{0}C)	Statistical Parameters / Constants		
	R^2	n	K_f (mg/L)
30^{0}C	0.964	0.8741	4.720
40^{0}C	0.968	0.7905	3.572
45^{0}C	0.957	0.7552	2.971
50^{0}C	0.969	0.7380	2.582
55^{0}C	0.973	0.6954	1.990
60^{0}C	0.972	0.6557	1.531

A value for n ranging between 0 and 1is a measure of surface heterogeneity, becoming more heterogeneous as its gets value closer to zero. Values of n for removal of dye by copper pod flower were 0.8741, 0.7905, 0.7552, 0.7380, 0.6954 and 0.6557 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 malachite green dye. Values of K_f for removal of dye by copper pod flower were 4.720, 3.572, 2.971, 2.582, 1.990 and 1.531 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= 0.957 to 0.973) compared to the Langmuir isotherm model. This indicates that the adsorption of malachite green dye on copper pod flower takes place as monolayer adsorption on the adsorbent surface, homogenous in adsorption affinity [18].

Tempkin isotherm

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

$$q_e = B\ (lnA + lnC_e) \quad (8)$$

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 lnC_e versus q_e and is shown in Figure 7. Values of B were in the range of 9.44 – 51.55, while values of A in the range of 0.1352 – 0.4456. The result shows that Tempkin adsorption isotherm was not applicable to explain the malachite green adsorption onto activated carbon [19].

Dubinin-Radushkevich isotherm (D – R EQUATION)

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

$$\ln qe = \ln Xm - \beta E^2 \quad (9)$$

Where, Xm 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, Xm and β can be calculated from the slope and intercept of the plot of E^2 versus ln qe gives a straight line and is shown in figure 8. The correlation coefficients (R^2), E, Xm and β values are listed in Table 8.

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

$$E = 1/ (2\beta)^{1/2} \qquad (10)$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorptions. If the energy of activation is, <8 kJ mol^{-1}, the adsorption is physisorption. If the energy of activation is 8 to 16 kJ mol^{-1}, the adsorption is chemisorption. The activation energy of adsorption decreases with increase of temperature from 30 to 60 ^{0}C. E is > 11 kJ mol^{-1} indicates the adsorption of malachite green onto prepared activated carbon is chemisorption in nature [20].

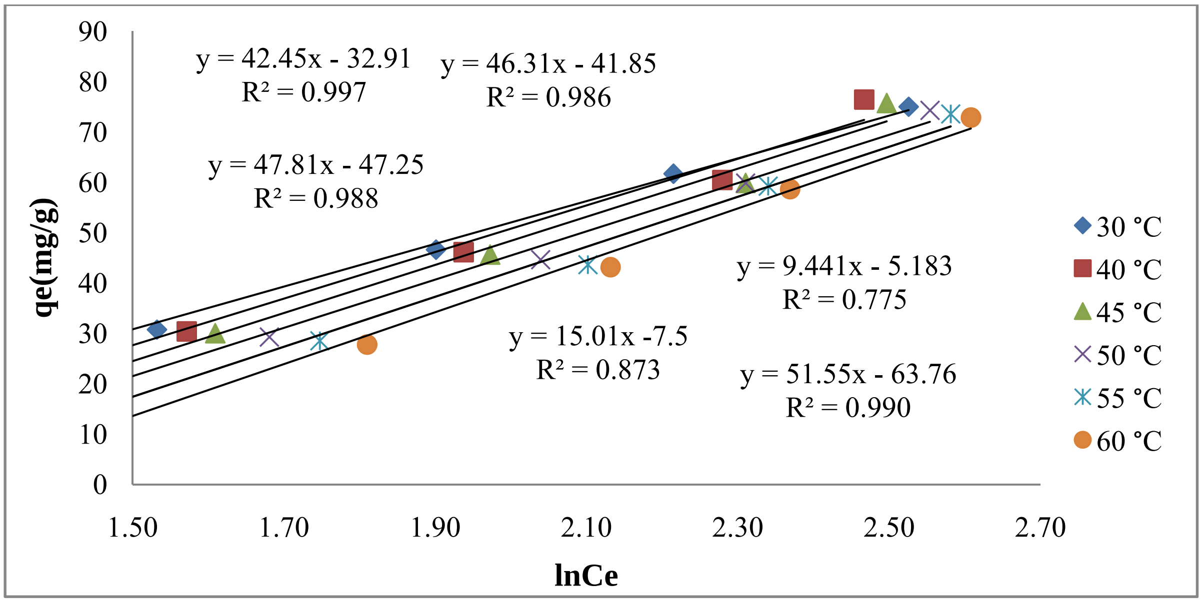

Figure 7. Tempkin isotherm for the adsorption of malachite green onto prepared activated carbon

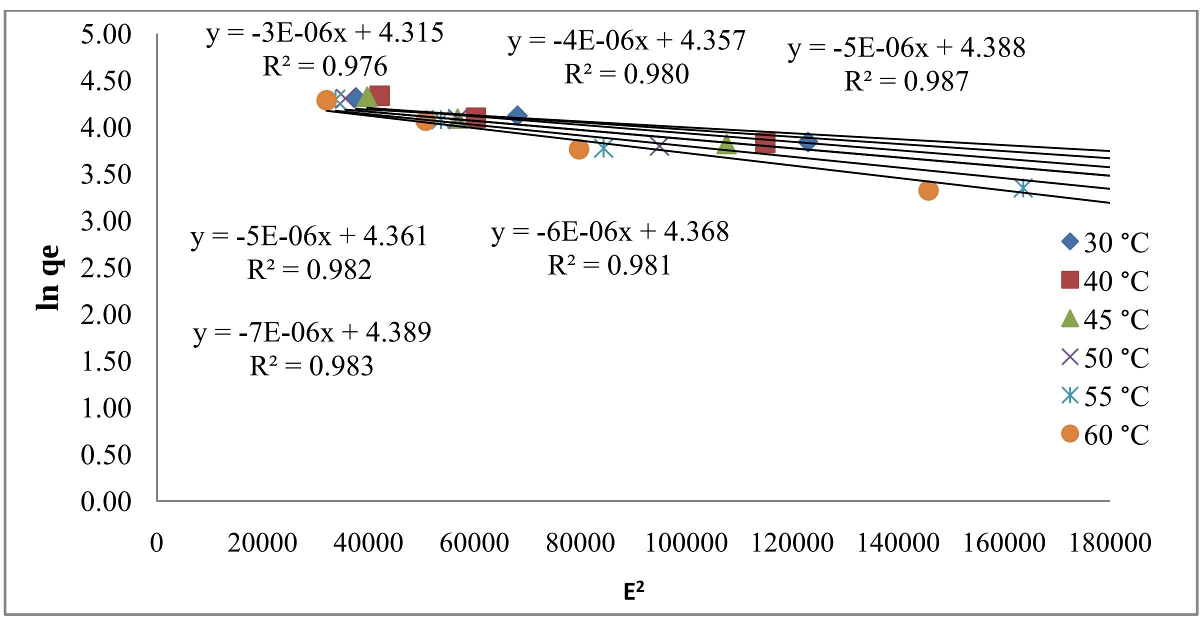

Figure 8. Dubinin -Radushkevich isotherm model for the adsorption of malachite green onto prepared activated carbon

Conclusion

The adsorption of malachite green dye from aqueous solution using copper pod flower as the low-cost adsorbent was investigated in batch process. The adsorption process was adsorbent dosage, contact time, initial metal ion concentration and pH dependent. The equilibrium adsorption isotherm data was best represented by Freundlich isotherm model better than Langmuir isotherm model. From the kinetic data, it was found that adsorption of malachite green dye using activated carbon is explained well by pseudo-second order kinetic model. Kinetic data results indicate that intraparticle diffusion is not only the rate limiting step of the adsorption process. 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. Finally, the results clearly indicated that copper pod flower could be used as an alternative to highly efficient low cost and abundant materials for removal of malachite green dye from contaminated aqueous solutions.

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