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Removal of malachite green dye in aqueous solution by Activated Custard apple (*Annona Squamosa*) Peel Powder

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Abstract

In the present study Custard apple peel powder (CAPP), a fruit waste, was activated by carbonizing in a Muffle Furnace to improve its surface adsorption capacity and used as an adsorbent for removal of Malachite Green (MG) from aqueous solution. Carbonisation of the bioadsorbent plays a key role in efficient adsorption which is proved by surface analysis of the bioadsorbent by Scanning Electron Microscope before and after adsorption. The color removal performance of CAPP has been investigated using parameters such as initial dye concentration (10-40ppm), pH (3-7), time of contact (15-90 min) and adsorbent dosage (0.1-0.6 mg/50ml). Adsorption was favorable at slightly acidic condition and the maximum removal was obtained at pH 6. Percentage of dye removal was maximum when the contact time was 75 min(91.5%) and adsorbent dosage of 0.3mg/50ml (95.3%). The kinetic studies revealed that the kinetic data fitted well to the pseudo-first-order model. The isotherm study also indicated that MG adsorption on CAPP matched well with the Langmuir model rather than the Freundlich model. The results show that CAPP can be a promising alternate for the removal of MG from aqueous solutions and effluents.

Keywords: Malachite Green, Custard Apple Peel Powder, Langmuir isotherm, Pseudo first order Model.

1. INTRODUCTION:

Dye is a natural or synthetic substance used to add a color to or change the color of a material. Dye industry is one of the quickly developing commercial industry because of development of materials like textile, ceramic and cosmetics. Colors are broadly utilized in industries like textile industries, printing industries, food Industries, cosmetic Industries, leather industries, paper industries and so forth [1]. The extensive use of dyes often poses pollution problems in the form of colored waste water discharged into stream, pond, river and various natural sources of water. Dyes usually have a synthetic origin and complex aromatic structure. They are more stable and difficult to biodegrade [2]

Malachite green(MG) is a popular dye which finds applications in various fields .In aquaculture industry, MG is extensively used as biocide against parasitic treatment and for fungal and bacterial infections in fish and fish eggs due to its potent anti-parasitic effect [3]. It is also widely used in various industries like silk, wool, jute, leather and paper to color their products [4].In addition to its vast application ,it induces risk of cancer, acts as a liver tumor-enhancing agent also. The dyes check the biological activity in aquatic lives. They negatively affect mutagenic and carcinogenic characteristics [5,6] and cause severe effects on nervous system, reproductive system, liver, brain and kidney. Various types of waste water treatment methods are ion exchange, activated carbon, filtration, electrolysis and reverse osmosis which requires high capital investment and operational costs. Interestingly, biosorption was known to be a low-cost method for the treatment for dye-containing wastewater [7]. This technique has attracted most of the researchers because of its low initial cost, flexibility and simplicity of design, ease of operation, reusability of biosorbent and high efficiency. Low cost bioadsorbents like water hyacinth[8], rice husk[9], saw dust[10], leucaena leucocephala[11], almond shell [12] etc are reported by literature for their efficiency and successful usage in the removal of MG dye from aqueous solutions. Present study mainly focusses on the removal of MG from aqueous solution by making use of activated custard apple peel powder as potential adsorbent.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbent:

The custard apple peels used in this study were collected from local Fruit market. The collected biomass material was extensively washed with tap water to remove soil, colored matter and dust, then washed with double distilled water then dried in an hot air oven at 80^0 C to attain a constant weight. These dried custard apple peels were first cut into small pieces and then crushed in a mechanical crusher to a constant powder size which were then sieved to 400µm. The powdered samples were stored in a vacuum desiccator till further use.

Activation of the adsorbent by carbonation:

The adsorbent powder was activated by carbonising in a muffle furnace at 300^0C for one hour in order to produce charcoal. The adsorbent is cooled and stored in an air tight container for the further use.

Figure 1: Carbonised Custard apple Peel Powder

2.2 Preparation of adsorbate

In the present study Malachite Green dye (mol. formula $C_{23}H_{25}N_2Cl$, mol. weight = 364.92, λ_{max} = 617 nm) obtained from HiMedia Laboratories Pvt.Ltd, Mumbai was used without further Purification. .A Stock solution of 500 mg/L was prepared with double distilled water. All working solutions used in tests were prepared by appropriately diluting the stock solution to a pre-determined concentration. All other chemicals used in this study were analytical reagent grade.

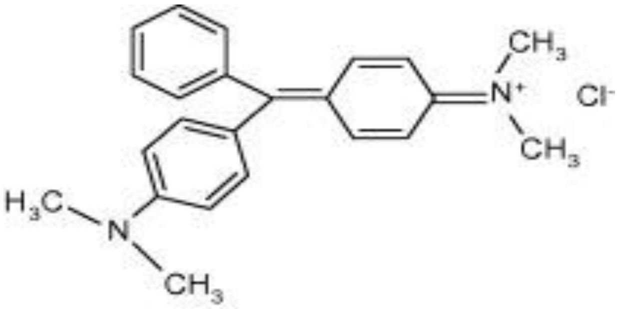

Figure 2: The structure of Malachite Green

2.3 Adsorption studies

The adsorption experiments were carried out by agitating 0.2g of activated **Custard Apple Peel Powder** (CAPP) into 50 ml of dye solution of desired concentrations in a 250ml stoppered reagent bottle at 350 RPM in an orbital shaker. Residual dye concentration in the supernatant liquid was found out by measuring the absorbance of the dye using a UV-VIS spectrophotometer (PerkinElmer UV-VIS Spectrophotometer) at 617nm. Amount of dye adsorbed per gram of the adsorbent can be given as follows.

$$\mathbf{qe} = \frac{(Co - Ce)V}{W} \qquad (1)$$

where, C_0 is the initial concentration of malachite green (mg/l), C_e is the equilibrium concentration of dye (mg/l), V is the volume of the solution (l) and w is the mass of CAPP (g).

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characteristics:

The Scanning Electron Microscopy (Model JSM-638OLA) images of CAPP before and after the adsorption of malachite green dye is shown in fig. 3(a) and 3(b) respectively. From figure 3(a) it is evident that the adsorbent surface has large number of prominent pores of average diameter 1.27 µm which are the actual sites of dye adsorption. Fig 1(b) shows the adsorbent surface after adsorption where the dye molecules are trapped in the pores to give plane surface as shown below.

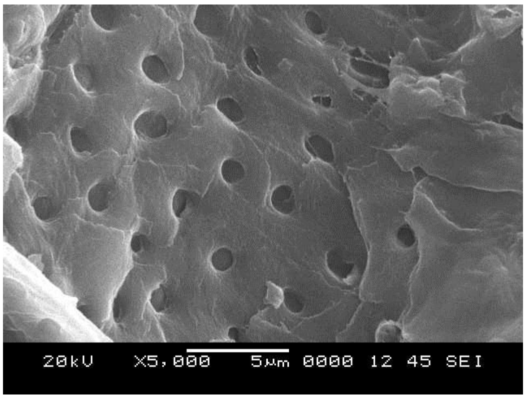

Figure 3(a): Before Adsorption

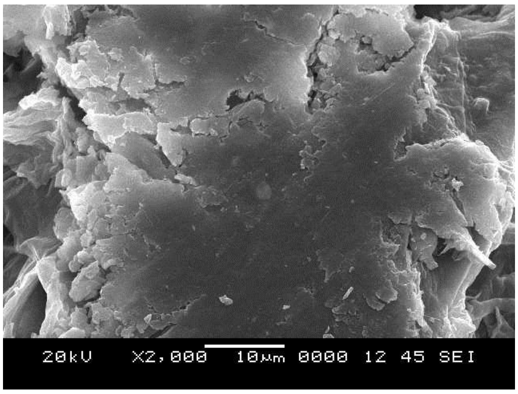

Figure 3(b) : After adsorption

3.2 Effect of Initial Dye concentration:

The effect of initial dye concentration was analysed by taking 50ml of MG solution of varying concentration. 0.2g of CAPP is added to 50ml of MG solution with varying initial concentration (10,15, 20, 25, 30, 35 and 40 ppm). At the end of each adsorption test, sample was centrifuged and the concentration of residual MG in the supernatant solution was analyzed using a UV-VIS spectrophotometer by monitoring the absorbance at 617 nm. Fig.(4) shows that as initial concentration of the MG dye is increased from 10ppm-30ppm, markable increase in dye adsorption is observed as it improved number of collisions between dye molecules and CAPP particles. Percentage of dye removal becomes almost constant after a concentration of 30ppm as the adsorbent surface becomes saturated because of dye adsorption which is in well agreement with literature [13],[14].

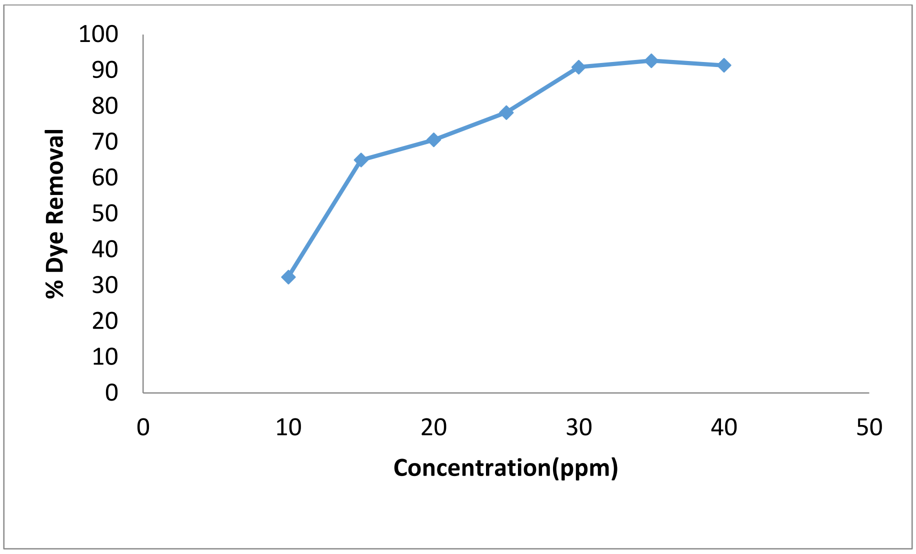

Figure 4: Effect of dye concentration on colour removal of MG by CAPP

3.3. Effect of pH:

The effect of solution pH was studied for adsorption of malachite green at room temperature with constant initial concentration of 20 ppm .The range of solution pH was adjusted between 3 and 7 by using 0.1N NaOH and 0.1N HCl. Figure 3 depicts the effect of pH on the adsorption of Malachite green onto the CAPP adsorbent. It was observed that the percentage of dye removal was lower at lower pH for cationic dyes like MG due to high concentration of H^+ ions which competes with the cationic groups [15,16] and as the pH increases, the attraction between positively charged dye and adsorbent increases and hence the removal efficiency increases as reported by [17] The adsorption capacity increases from pH 3-7 as shown in the figure.[5]

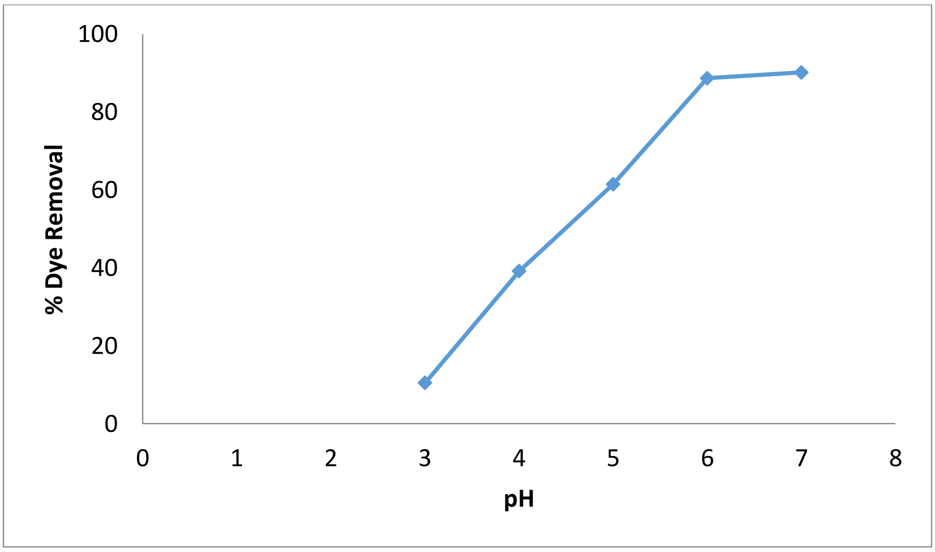

Figure 5: Effect of pH on Colour Removal of MG by CAPP.

3.4 Effect of adsorbent dose:

The removal of Malachite green dye by CAPP was analyzed by changing the quantities of sorbents (0.1g, 0.2g, 0.3g, 0.4g, 0.5g and 0.6g) for 50 cm^3 of dye solution with initial dye concentration of 20 ppm. Contact time of the sorbent and pH also were kept constant to study only the effect of adsorbent dose. It was found that percentage of dye removal increased with increase in the adsorbent dose upto 0.3g and then onwards it became constant as equilibrium is assumed to be achieved after 0.3 g absorbent. It is basically due to saturation of the active site which does not allow further absorption to take place Our observations match with those already reported in the literature.[18]. Variation of percentage of dye removal Vs Adsorbent Dose is shown in figure 6

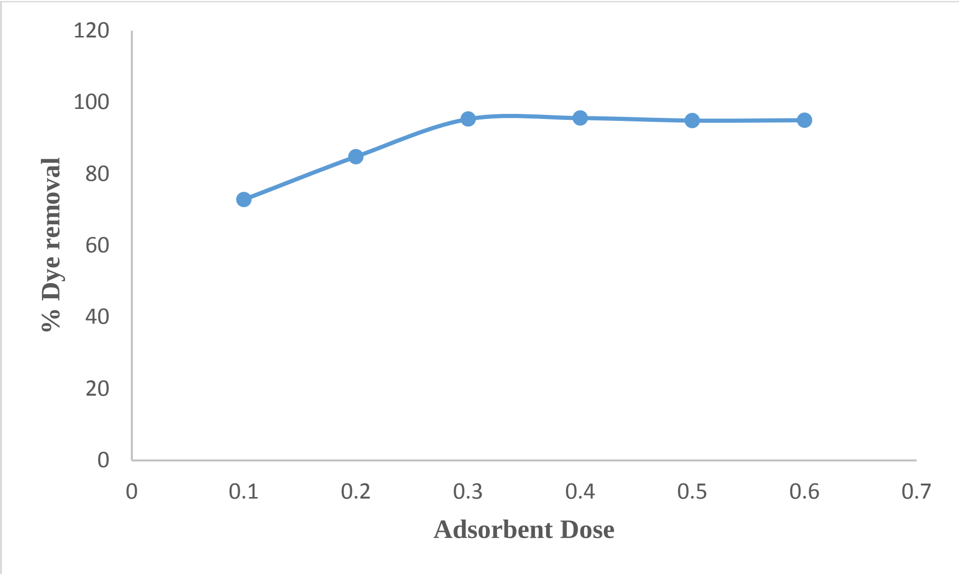

Figure 6: Effect of Adsorbent Dosage on Colour Removal of MG by CAPP

3.5 Effect of Contact time

The percentage reduction of colour with contact time (15- 90 min) at an optimum adsorbent dose of 0.2 g and agitation speed 350 rpm is shown Figure 7 . The results revealed that the rates of percentage colour removal goes on increasing with adsorbent dose as the adsorbent sites are used by increasing number of adsorbent molecules. Further, as contact time increased, the colour removal percentage becomes almost constant as surface adsorption sites become exhausted and the uptake rate is controlled which is in accordance with literature. [19] It may be found that an optimum contact time at which maximum colour removal achieved is 75 min. and the colour reduction percentage is 91.5.

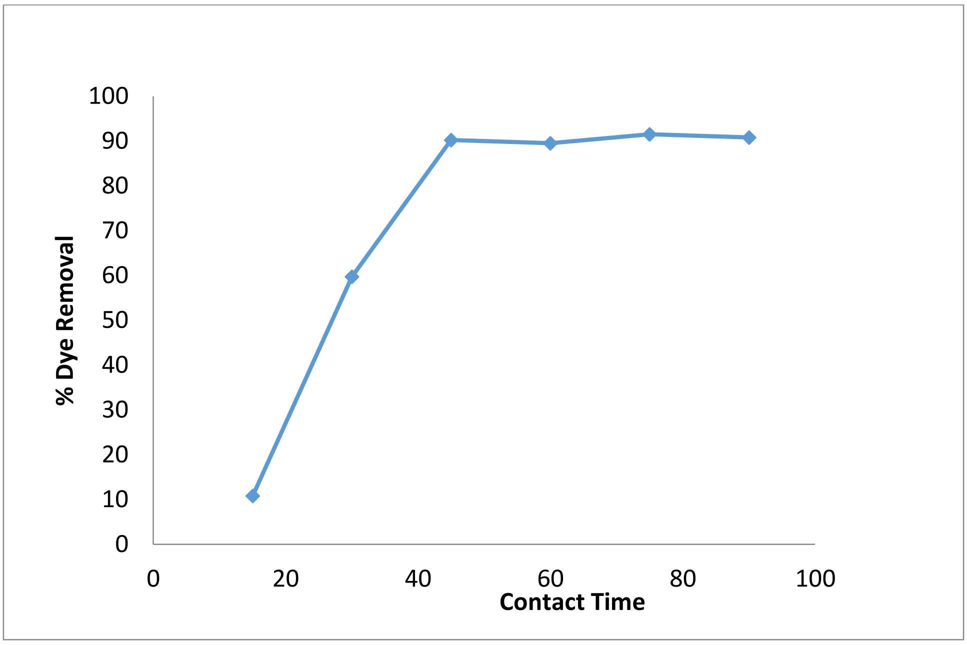

Figure 7: Effect of Contact Time on Colour Removal of MG by CAPP.

4. ADSORPTION ISOTHERMS:

The adsorption isotherm indicates the way the adsorption molecules distribute themselves between the solid phase and liquid phase when the adsorption process reaches the equilibrium state. Adsorption isotherm is basically important to describe interaction of solute with adsorbents and is critical in optimizing the use of adsorbent. Two well-known models, namely Freundlich and Langmuir isotherms, were selected to explicate dye–adsorbent interaction in the present study. The applicability of the isotherm equation is compared by judging the correlation factor R^2 [20]

4.1 Freundlich s Adsorption isotherm:

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centres of the adsorbent. The well-known expression for the Freundlich model is given as [21]

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (2)$$

where qe is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, 1/n is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and Ce is the equilibrium concentration (mgL-1). The values of Kf and 1/n can be obtained from the slope and intercept of the plot of log qe against log Ce.

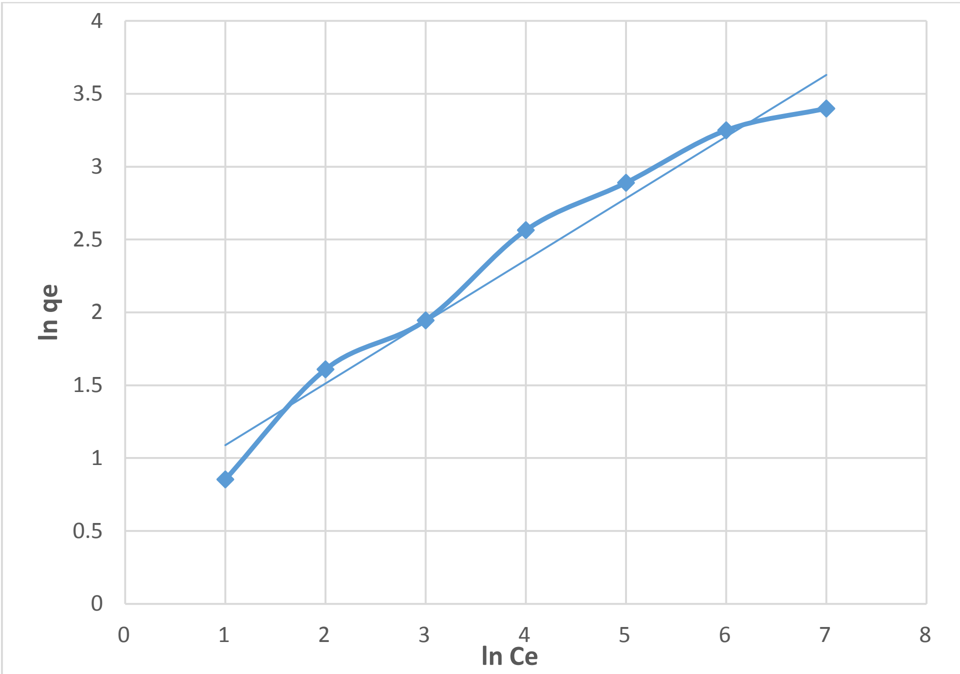

Figure 8: Freundlich isotherm for the adsorption of Malachite green on CAPP.

4.2 Langmuir Adsorption Isotherm:

The Langmuir isotherm model is based on the assumption that there is a finite number of active sites which are homogeneously distributed over the surface of the adsorbent These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules .

The linear form of the Langmuir equation can be expressed as

Ce /qe = Ce/qm + 1/(qm.b) (3)

where qe is the amount of dye adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (mgL-1), and qm and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg).

According to Equation 3, when the adsorption obeys the Langmuir equation, a plot of Ce /qe versus Ce should be a straight line with a slope of 1/qm and intercept 1/qm.b [22]. This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L [23], which is defined as

$$R_L = \frac{1}{(1 + b_L.Co)}$$

The R_L value in the experiment (R_L= 0.4055) indicates that the type of adsorption is favorable (0 <RL<1). Higher correlation coefficient (R^2) values of the straight lines obtained confirms the validity of Freundlisch adsorption isotherm. The results are depicted in figure 10.

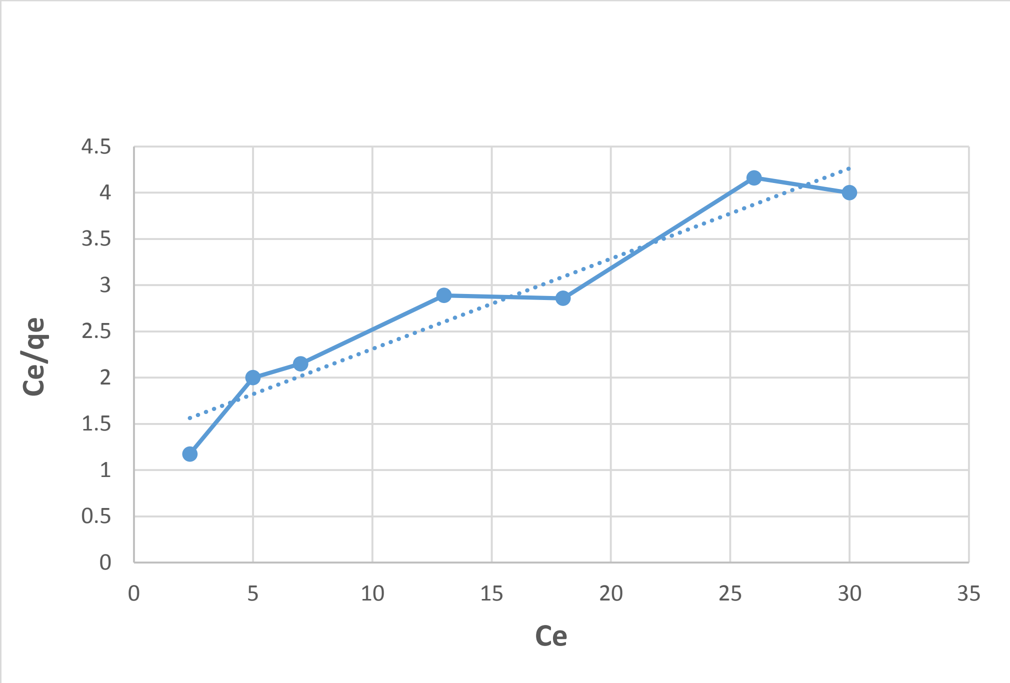

Figure 10: Langmuir isotherm for the adsorption of Malachite green on CAPP.

Adsorption constants of freundlisch and Langmuir models are listed in Table 1.

Table.1: adsorption isotherm parameters of MG onto CAPP

Freundlich s Constants			**Langmuir Constants**			
n	**Kf**	**R^2**	**Q_m**	**b**	**R^2**	**R_L**
2.3602	**1.94 (mg/g)**	**0.9667**	**10.23**	**0.0733**	**0.9301**	**0.4055**

5. ADSORPTION KINETICS

To understand the nature of adsorption type, rate and capacity of adsorption process adsorption kinetics study was studied. Kinetic studies are important for designing and optimizing the biosorption system. In the present work, kinetic study of dye removal was conducted using 50 mL of dye solution (20ppm) at various contact times (10-60 min) and at a stirring speed of 350 rpm [24]. For evaluating the adsorption kinetics, Pseudo-First Order and Pseudo-Second Order Models are considered in the present study.

5.1 Pseudo-first-order Model:

The linear form of pseudo- first order model is represented by equation 4.

$$\text{Log (qe-qt)=log qe} - \frac{K1}{2.303}\,t \qquad (4)$$

where qt (mg g^{-1}) is the amount of dye adsorbed at time t. qe (mg g^{-1}) is the adsorption capacity at equilibrium,K_1 (min^{-1}) is the pseudo first order rate constant, and t is the contact time (min).

The values of K_1 (rate constant) and qe are calculated from the linear plots of log(qe-qt) versus t,(figure 11) for the adsorption of dye. The values of the constants K1,qe and R^2 are listed in table 2. It is evident from the results of R^2 that pseudo first order model is best fitted to the present dye- adsorbent interaction.

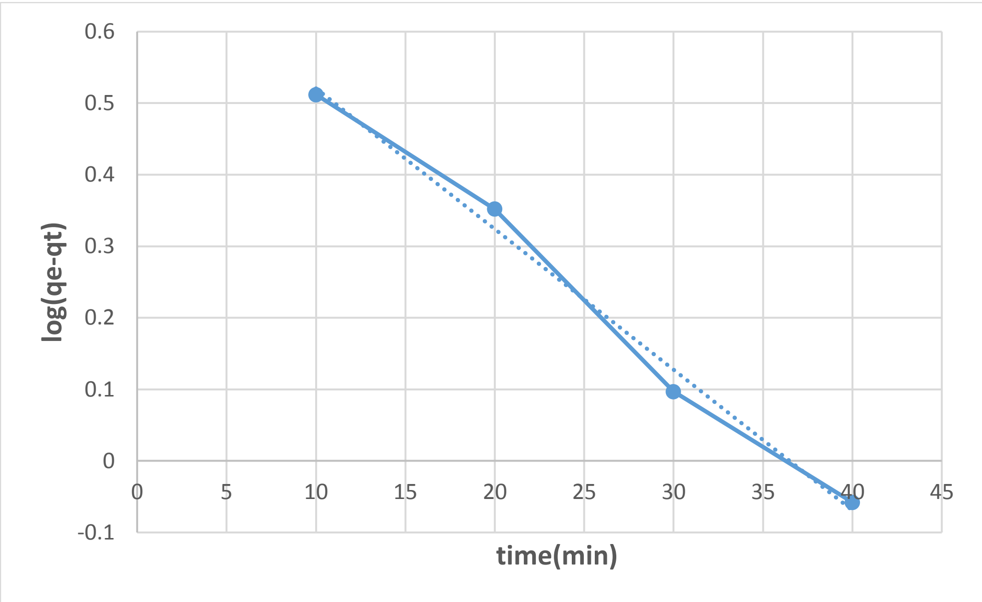

Figure 11: Applicability of Pseudo first order rate model for the adsorption of MG on CAPP.

5.2 Pseudo second order model

The pseudo second-order model, which has been applied for analyzing adsorption kinetics rate is given by equation

$$t/q_e = 1/K_2q_e^2 + (1/q_e)\,t \qquad (5)$$

Where t is the contact time (min), qe (mg/g) is the amount of the solute a adsorbed at equilibrium, the slope and intercept of the plot t/qe versus t,(figure 12) are used to calculate qe and K_2 (adsorption constant) . Values of constants K_2,qe and R^2 are presented in table 2.

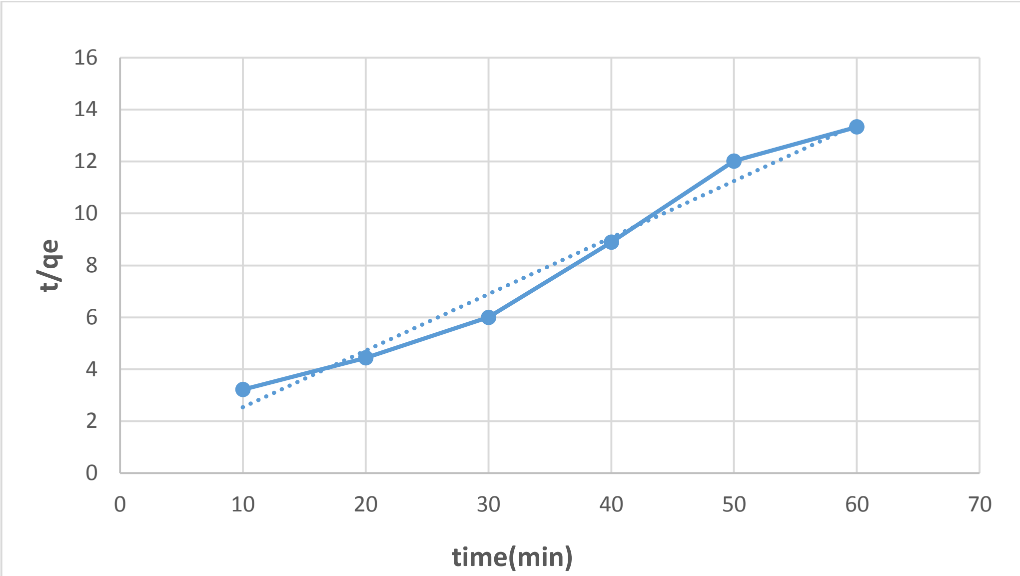

Figure 12: Applicability of Pseudo Second order rate model for the adsorption of MG on CAPP

5.3 Intra Particle Diffusion Model

During the adsorption experiments the spontaneous diffusion and stirring provide the transport of dye molecules from the bulk into the pores of the adsorbent, as well as adsorption at the outer surface of the adsorbent. The rate-limiting step may be either film diffusion or intra-particle diffusion. As they act in series, the slower of the two will be the rate determining step. The possibility of Malachite Green to diffuse into the interior sites of the CAPP was tested with Weber-Morris equation, known as intra-particle diffusion model [25,26] It includes an empirical function relationship common to most adsorption process in which the quantity of the adsorbed substance varies almost proportionately with t1/2 according to the following equation.

$$qt = k_i\, t^{1/2} + C \qquad (6)$$

where ki is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$) , qt (mg g^{-1}) is the amount of dye adsorbed at time t. The plot of qt versus $t^{1/2}$ should be a straight line with a slope ki and intercept C. Thickness of the boundary layer can be calculated by knowing the value of C. Boundary layer effect will be higher when C is greater. In the present study since plot does not pass through the origin ,the rate limiting process is either film diffusion or intra particle diffusion, . As they act in series, the slower of the two will be the rate determining step

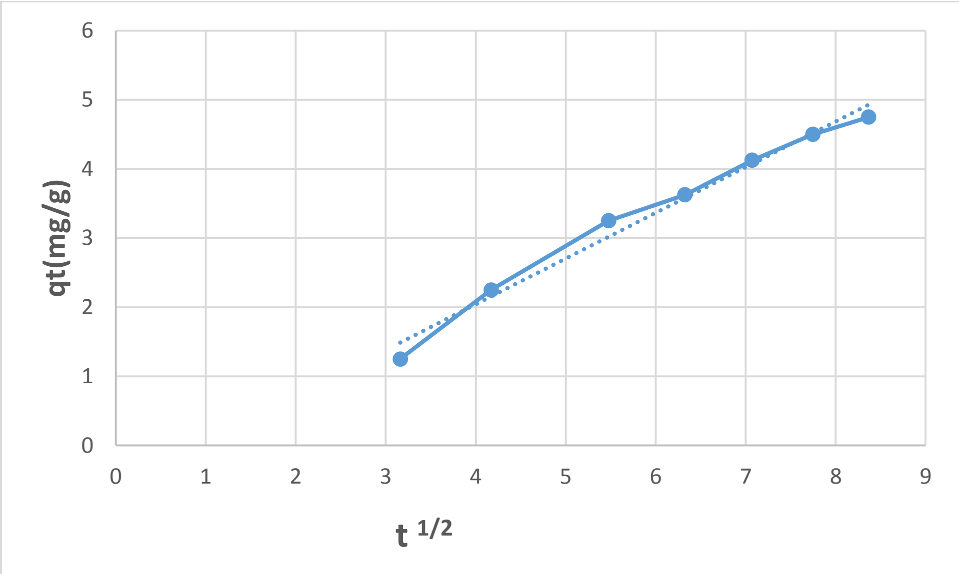

Figure 12: Applicability of Intra particle Diffusion model for the adsorption of MG on CAPP

Table 2: kinetic model parameters for pseudo first order, pseudo second order and intra particle diffusion model.

Pseudo first order model			Pseudo second order model			Intra particle Diffusion Model		
K_1	qe	R^2	K_2	qe	R^2	Ki	R^2	C
0.04	5.199	0.9901	0.1298	4.5	0.9767	0.6611	0.9837	0.6037

CONCLUSION

In the present study adsorption characteristics of Malachite green dye onto CAPP was investigated. Highest removal percentage of malachite green dye by CAPP is achieved at low acidic condition and also by taking 0.3 g of adsorbent per 50 ml of dye solution. The adsorption behavior was better described by Freundlich s isotherm model than the Langmuir model and the calculated adsorption capacities were 1.94mg/g. The kinetics of malachite green dye adsorption followed pseudo first order model. It has also been shown that CAPP acts as better adsorbent for the removal of turbidity from the sewage water .Present study shows good utilization of bio waste by which one can achieve a reduction of investment and raw material cost and can contribute to reuse of biowaste. Thus the commercially available adsorbents can be effectively replaced by low cost adsorbents.

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