

# **Adsorption of Malachite Green onto Chemically Activated Carbon Prepared from Waste Biomass**

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**ABSTRACT:** Activated carbon particles were prepared from industrial waste biomass using pyrolysis followed by chemical activation method with sodium hydroxide. The activated carbon was applied for the adsorption of malachite green (MG) dye from aqueous solution. The prepared adsorbent was characterized by FT-IR, BET surface area analysis, FE-SEM, zero-point charge and surface functionality. The surface area of the biomass chemical activated carbon (BCAC) was 67.12 m<sup>2</sup>/g. The adsorption of MG onto BCAC was studied as a function of aqueous phase pH, adsorbent dosage, different initial dye concentrations and contact time. The maximum dye adsorption occurred at neutral pH. The adsorption of MG onto BCAC was further investigated by Langmuir, Freundlich and Temkin isotherms. The maximum monolayer adsorption capacity was found 165.29 mg/L and it follows Langmuir adsorption isotherm model. Kinetic data were tested with pseudo-first-order and pseudo-second-order rate equations. The adsorption follows pseudo second order rate kinetics.

**KEYWORDS:** chemical activated carbon, isotherms, kinetics, adsorption, malachite green dye.

## **I INTRODUCTION**

Malachite green is a basic and water soluble cationic dye. Cationic dyes are widely used in dyeing of silk, wool, cotton, leather, jute, and paper. The leather and textile industries produce large quantities of wastes due to the usage of many chemicals in the processes. This poses a huge threat to the environment. Approximately 10,000 different types of dyes and chemicals are manufactured and about 7×10<sup>5</sup> tons of dye is being consumed worldwide. Roughly about 10 to 15% of these dyes enter into the nearby aquatic environment such as rivers, lakes and seas [1]. Most of the dyes cause allergic reactions, skin irritation, cancer, and mutation. Mainly malachite green on contact with skin causes irritation with redness and pain. It has been reported that if it gets into contact with eye, it can lead to permanent injury in human beings and animals. Though it is categorized as carcinogen, many industries still continue to use malachite green dye owing to its physico-chemical and biological properties [2–4]. Therefore, it becomes highly essential to remove such a toxic dye from wastewater stream before it enters into the aquatic environment.

Many methods are available for the removal of dyes from wastewater such as coagulation, solvent extraction, catalytic degradation and chemical oxidation [5, 6]. But these methods have some drawbacks. Among these methods, adsorption technology is one of the attractive methods due to its salient features such as cost effectiveness, efficiency, eco-friendliness and ease of recovery [7]. Many industries are employing adsorption technique and prefer to use activated carbon for the removal of various pollutants from effluents. This is because of the high adsorption control, highly porous nature of the material and high surface area. The activated carbon can be prepared using chemical activating agents such as H<sub>3</sub>PO<sub>4</sub>, NaOH, KOH, H<sub>2</sub>SO<sub>4</sub> or ZnCl<sub>2</sub>. Activated carbon has been used for various industrial applications. Activated carbon has also been used for the adsorption of H<sub>2</sub>S [8], dyes [9, 10]. Commercial activated carbons are available in market for adsorption of colour from various effluents. However, its usage is restricted due to high cost and difficulty in regeneration [11, 12]. Therefore, non-conventional adsorbent materials are need of the hour.

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Activated carbons prepared from agriculture waste and waste materials from the industries are considered to be more economical for wastewater treatment. Various agricultural waste based carbonaceous materials such as garlic peel [13], sugarcane bagasse [14], coconut shell [15], rice husk [16], fruit stones [17, 18], coir pith [19], orange peel [20], olive stones [21] and date pits [22] are used in the production of activated carbon. But the preparation of carbon from the materials mentioned above is somewhat difficult as it requires controlled experimental conditions. In the recent years, generation of solid waste by the process industries has increased manifold due to rapid industrial growth. Hence research initiatives for solid waste management are essential to control the environmental pollution.

The industrial solid waste could be converted into valuable materials such as activated carbon particles which may find varied applications. The carbon particles can be prepared from industrial waste biomass through pyrolysis followed by chemical/physical activation methods. The present study is focussed on the preparation of carbon particles by pyrolysis followed by chemical activation. The prepared activated carbon particles are well characterized and applied for the removal of a model pollutant, malachite green dye from the aqueous phase.

## II. MATERIALS AND METHODS

### A. Materials

Malachite green, an odourless dark green crystal with a chemical formula of  $C_{23}H_{25}N_2 \cdot C_2HO_4 \cdot 0.5C_2H_2O_4$  and molecular weight of 463.50 g, was purchased from S.D. Fine. Chem. Ltd, Mumbai. NaOH was purchased from Himedia laboratories Pvt, Mumbai. All the chemicals were used without further purification.

### B. Preparation of activated carbon

The solid waste biomass collected from tannery process which was washed and dried under sunlight. The dried biomass was carbonized at 500°C for 3 hours under inert atmosphere. The carbonised biomass was powdered and stirred with NaOH for 2 h. The slurry was then dried overnight at 110°C. After drying, the mixture was activated between 500°C and 700°C for 2 h under  $N_2$  flow. The prepared BCAC was washed and dried at 110°C for 12 h.

### C. Characterization studies

The BCAC was characterized using Fourier transform infrared (FT-IR) spectroscopy. Spectra were recorded between 400-4000  $cm^{-1}$  using Perkin Elmer FT-IR spectrometer. The progress of the adsorption experiments was monitored by measuring the absorbance of the aqueous phase before and after adsorption at  $\lambda_{max}$  616 nm using Shimadzu UV 2600 Japan spectrophotometer. The surface morphology of BCAC was characterised using Field Emission-Scanning Electron Microscope (FE-SEM) of Model Supra 55-Carl Zeiss, Germany. The surface area was calculated using Belsorb-mini II (Japan) at -77 K under nitrogen atmosphere.

## III. RESULTS AND DISCUSSION

### Characterization of BCAC

The Fig. 1(a) shows FT-IR spectrum of BCAC and their corresponding functional groups. In this Fig 1(a) a broad band at 3469  $cm^{-1}$  indicates the stretching vibration of hydroxyl group, and at 2921  $cm^{-1}$  explains the C-H stretching vibration. The sharp C=C and C-C stretching vibration band appear at 1640  $cm^{-1}$  and 1428  $cm^{-1}$ . The stretching vibration of C-O is found at 1105  $cm^{-1}$ . Fig. 1(b) represents the FE-SEM image of BCAC. The image illustrates the porous nature and rough surface morphology of the material.

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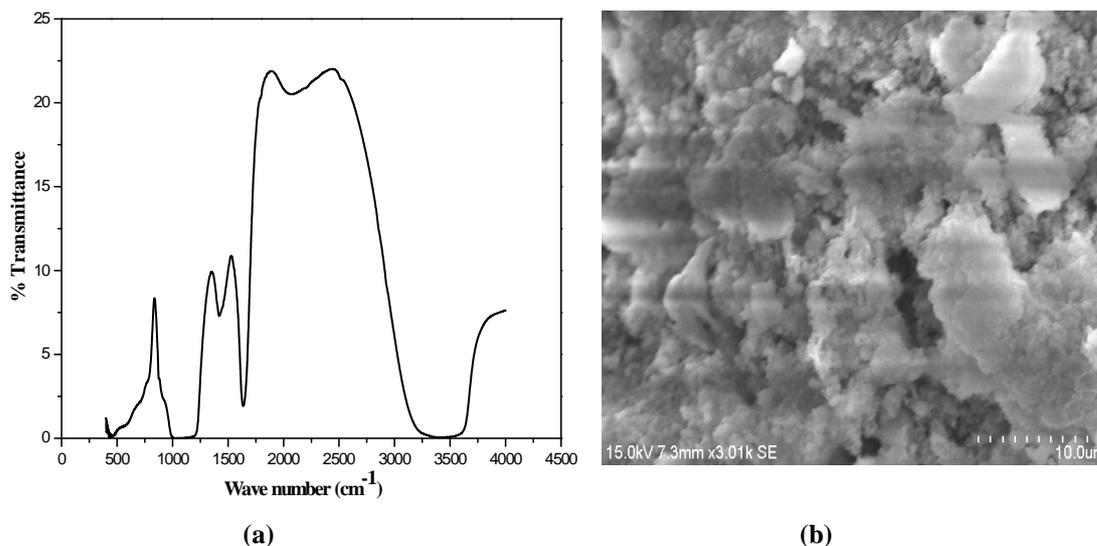


Fig. 1. (a) FT-IR spectrum and (b) FE-SEM micrographs of BCAC

The surface area of BCAC was found to be  $67.12 \text{ m}^2/\text{g}$ . The zero point charge of the BCAC adsorbent was 10.21. The surface of BCAC was found possess more basic functional groups ( $0.331 \text{ m}_{\text{eq}}/\text{g}$ ) than acidic functional groups ( $0.063 \text{ m}_{\text{eq}}/\text{g}$ ).

## IV BATCH EXPERIMENTS

### A. Effect of initial aqueous pH on adsorption

Initial aqueous phase pH plays an important role in the liquid-phase adsorption process, particularly on the adsorption capacity. The pH of the dye solution affects its structural stability and its colour intensity. Effect of aqueous pH was determined by varying the initial aqueous phase pH in the range of 2 to 12 by the addition of HCl and NaOH. It was found that there is no significant change in the adsorption of MG with varying pH. However, maximum adsorption occurred is 97.00 % at neutral pH as shown in Fig. 2.

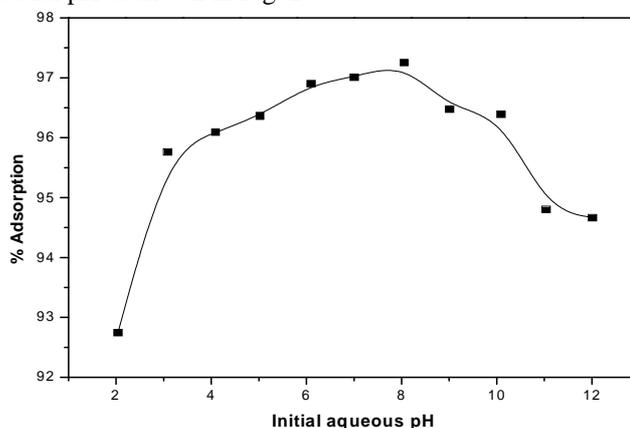


Fig. 2. Effect of initial aqueous pH for the adsorption of MG onto BCAC

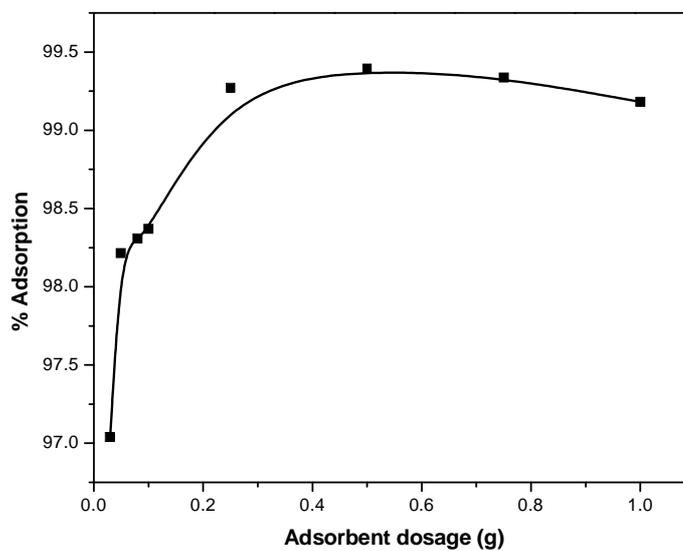
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### B. *Effect of adsorbent dosage*

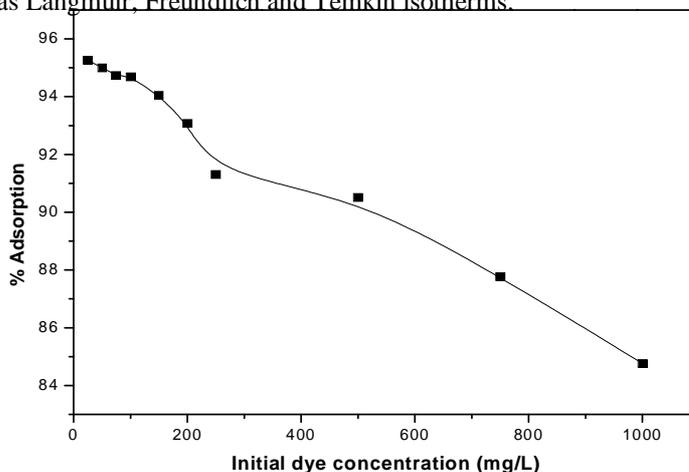
The effect of adsorbent dosage was studied by varying the adsorbent dosage from 0.01 g/10 mL to 1.0 g/10 mL. From Fig. 3, it is observed that the percentage adsorption of dye MG increased with an increase in the carbon dosage. The maximum % of adsorption of MG was found to be 98.21% at a dosage of 0.05 g/10 mL.



**Fig. 3. Effect of Adsorbent dosage for the adsorption of MG onto BCAC**

### C. *Effect of initial dye concentration*

The effect of initial dye concentration was studied by varying the initial MG dye concentrations from 25 mg/L to 1000 mg/L for the optimised adsorbent dosage. The results were shown in Fig. 4. The % adsorption decreased with an increase in the initial MG concentration. This study was further extended to calculate equilibrium parameters using isotherm models such as Langmuir, Freundlich and Temkin isotherms.



**Fig. 4. Effect of initial dye concentration for the adsorption of MG onto BCAC**

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### D. Adsorption isotherms studies

#### D(i). Langmuir isotherm

The Langmuir equation is applicable to homogeneous adsorption and it is based upon the assumption of monolayer adsorption, where the adsorption of each adsorbate molecule on to the surface has equal sorption activation energy.

The linear form of this isotherm is represented by the expression [23]:

$$\frac{1}{q_e} = \frac{1}{q_0 K_L C_e} + \frac{1}{q_0} \quad (1)$$

Where,  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively.  $K_L$  (L/g) is the Langmuir equilibrium constant and the maximum monolayer adsorption capacity ( $q_0$ ) was found to be 165.29 mg/g which is higher than that reported in literature [24].

#### D(ii). Freundlich isotherm

The most important multisite adsorption isotherm for the non-ideal adsorption on heterogeneous surfaces is the Freundlich adsorption isotherm and the linear form of this isotherm is expressed as [25]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where,  $K_F$  (L/g) is the Freundlich constant and  $n$  (g/L) is the Freundlich exponent. The adsorption of MG onto BCAC is favourable when 'n' lies between 1 and 10. A plot of  $\log q_e$  versus  $\log C_e$  shows that the constant  $K_F$  equals 6.329 and exponent  $n$  equals 1.376.

#### D(iii). Temkin isotherm

The Temkin isotherm model describes the behaviour of adsorption systems on heterogeneous surfaces, which takes into account the interactions between the adsorbate and the adsorbent. The linear form of this isotherm is [26]:

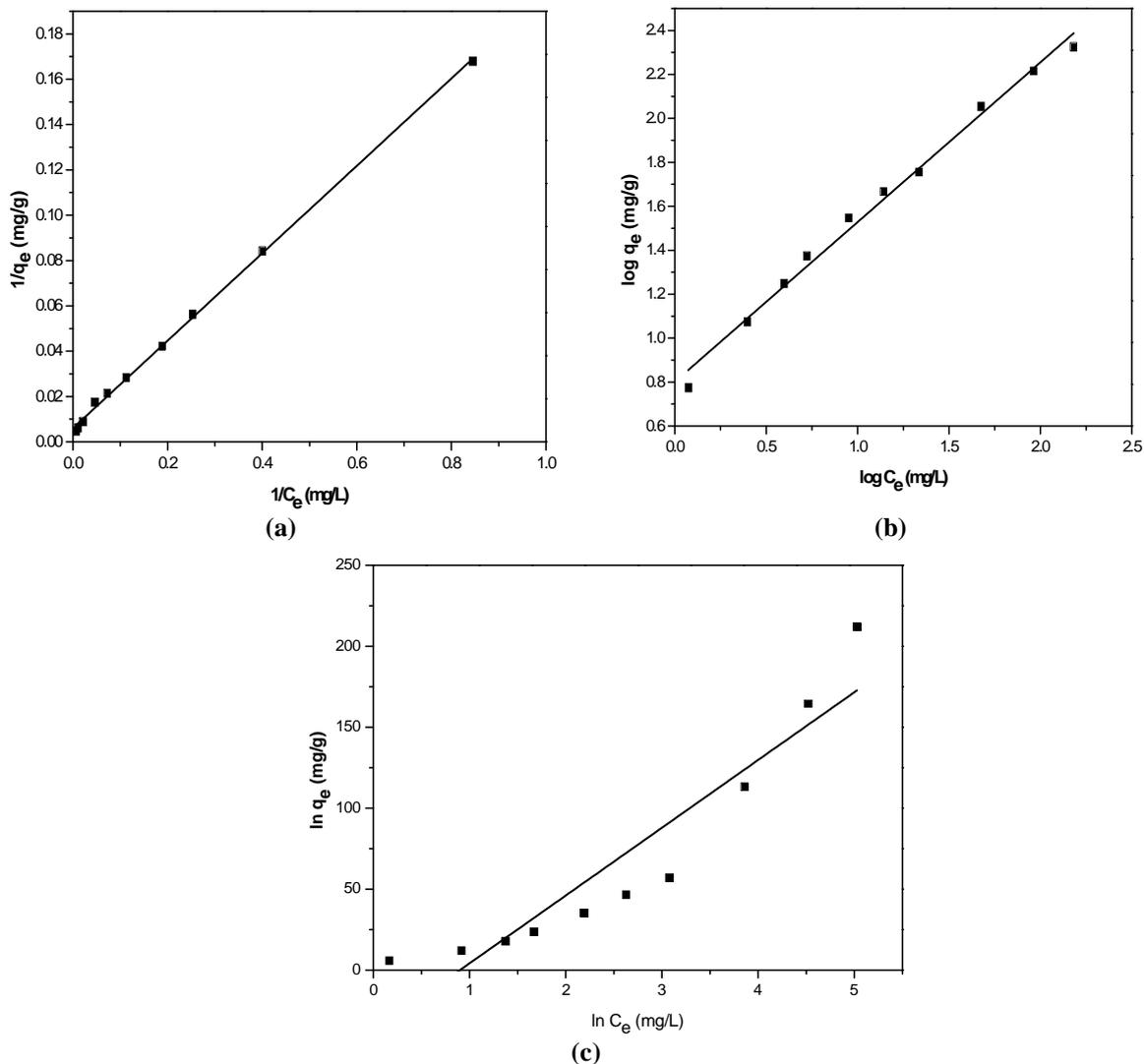
$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3)$$

where,  $B_1 = RT/b$ .  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant ( $J \text{ mol}^{-1} \text{ K}^{-1}$ ),  $b$  is the Temkin constant related to the heat of adsorption and  $K_T$  is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy.

The Langmuir, Freundlich and Temkin isotherm plots are shown in Fig. 5(a), 5(b) and 5(c). and the parameters obtained from these plots are given in Table 1.

**Table 1. Isotherm parameters for the adsorption of MG onto BCAC**

| Langmuir isotherm |        |       |        | Freundlich isotherm                                    |       |        | Temkin isotherm |       |        |
|-------------------|--------|-------|--------|--|-------|--------|-----------------|-------|--------|
| $K_L$             | $q_0$  | $R_L$ | $r^2$  | $K_F$  | $N$   | $r^2$  | $B$             | $A$   | $r^2$  |
| (L/g)             | (mg/g) |       |        | ( $\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$ ) | (g/L) |        |                 | (L/g) |        |
| 0.031             | 165.29 | 0.031 | 0.9986 | 6.329  | 1.376 | 0.9907 | 41.86           | 0.407 | 0.8619 |



**Fig. 5. (a) Langmuir isotherm, (b) Freundlich isotherm and (c) Temkin isotherm for adsorption of MG onto BCAC**

**E. Kinetics of Adsorption Process**

The kinetic data for the adsorption of MG with various initial concentrations were tested by the kinetic models namely pseudo first-order and pseudo second-order models. The kinetic experiments were carried out by withdrawing samples and analyzing their concentration at regular time intervals.

**E (i). Pseudo first-order model**

The linear form of pseudo first-order equation of Lagergren is generally expressed as follows [27]

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of adsorbed adsorbate at equilibrium and at time  $t$ , respectively.  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo first-order adsorption which can be found from the plot for  $\ln(q_e - q_t)$  versus  $t$ .

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**E(ii). Pseudo second-order model**

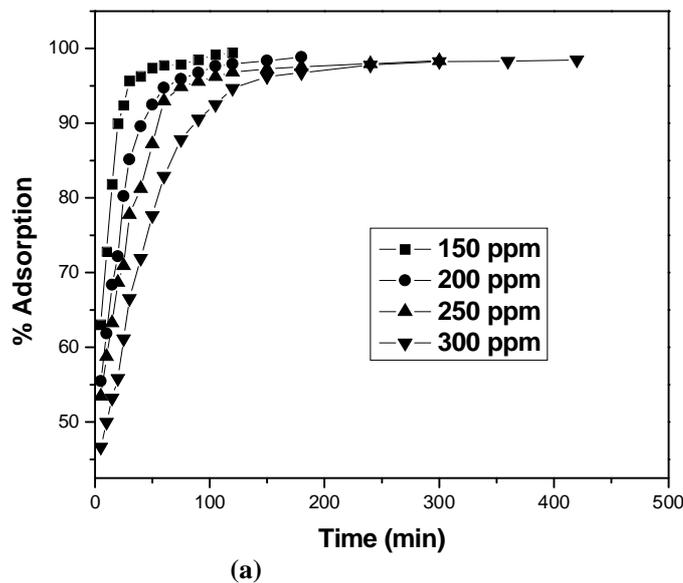
The linear form of pseudo second-order kinetic rate equation [28] is expressed as mentioned below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where,  $k_2$  (g/mg min) is the equilibrium rate constant of pseudo second-order adsorption process. If the pseudo second-order kinetic equation is applicable, the plot of  $t/q_t$  against  $t$  should give a linear relationship. The kinetic parameters obtained from the plots as shown in Fig (6) were tabulated in table 2. The  $r^2$  values of pseudo second-order model was closer to 1 when compared to the  $r^2$  values of pseudo first-order model. Therefore the kinetics for the adsorption of MG onto BCAC followed pseudo second-order model.

**Table 2. Kinetic parameters for the adsorption of MG onto BCAC**

| $C_0$<br>(mg/L) | Pseudo first-order kinetic equation |                                |         | Pseudo second-order kinetic equation |                                     |         |
|-----------------|-------------------------------------|--------------------------------|---------|--------------------------------------|-------------------------------------|---------|
|                 | $q_e$<br>(mg/g)                     | $k_1$ (1/min)<br>$\times 10^2$ | $r_1^2$ | $q_e$ (mg/g)                         | $k_2$<br>[g/(mg min)] $\times 10^3$ | $r_2^2$ |
| 150             | 7.869                               | 0.0427                         | 0.9111  | 30.58                                | 0.0111                              | 0.9998  |
| 200             | 16.35                               | 0.0321                         | 0.9738  | 40.49                                | 0.0046                              | 0.9998  |
| 250             | 17.54                               | 0.0221                         | 0.9178  | 50.76                                | 0.0026                              | 0.9998  |
| 300             | 28.35                               | 0.0174                         | 0.9740  | 61.35                                | 0.0013                              | 0.9994  |



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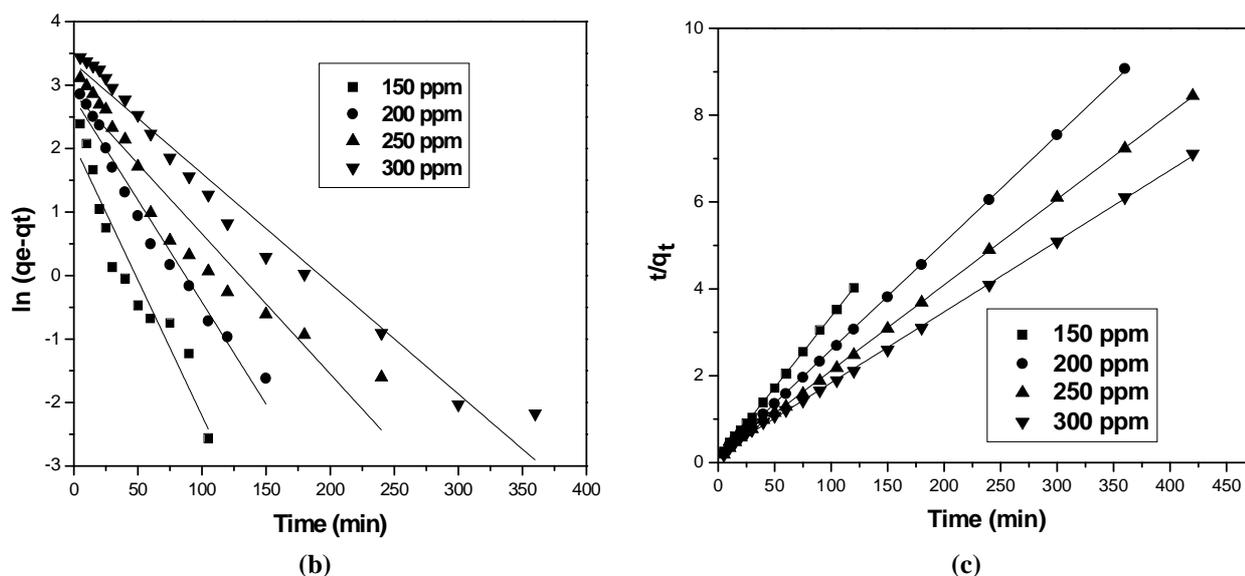


Fig. 6. (a) Percentage adsorption (b) pseudo first-order model and (c) pseudo second-order model for adsorption of MG onto BCAC

### V. CONCLUSION

The adsorbent BCAC was prepared from the industrial waste biomass and used for the adsorption of MG dye from aqueous phase. Preliminary batch adsorption studies were carried out at neutral pH. From the adsorption study, Langmuir isotherm fits well with the equilibrium data. The kinetics of adsorption follows pseudo second-order. Experimental results of the present investigation showed that BCAC is a potential adsorbent for the removal of MG from aqueous solution over a wide range of concentrations.

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