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# Adsorption Studies of Methylene Blue Dye on Cow Dung Based Low-Cost Adsorbent

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## Abstract

The available conventional methods for the treatment of colored waste water are expensive and produce large amount of sludge at the end of the process. In many methods, adsorption is known to be a promising technique. Commercially available activated carbon from coal used as an adsorbent material is an expensive and non-renewable has restricts its use. Adsorbent from agricultural wastes and plant biomass are considered to be low-cost candidates. The adsorption of methylene blue dye on low coast adsorbent cow dung was studied under various conditions such as, contact time, concentration of adsorbate etc. Batch adsorptions experiments for the equilibrium data were represented using Freundlich, Langmuir and Temkin adsorption isotherm models. The mechanisms of the adsorption process based on the correlation coefficient values suggest that cow dung adsorbents are best fitted into Temkin isotherm concludes electrostatic interaction between adsorbate and adsorbent. It was observed that under current experimental conditions cow dung adsorbent is efficient for removal of dyes (~90 %) from the aqueous solutions. Thus, it discusses the potential of utilizing cow dung as a cheap and effective adsorbent.

**Keywords:** Batch adsorption, Cow dung, adsorption isotherm, colored effluent, methylene blue,

## Introduction

The colored effluent such as presence of methylene blue dye is toxic to human body as well as harmful to aesthetic nature of the water surface [1,2].

Industries such as textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food release dyes effluents. The presence of dyes at very low concentrations in effluent is highly visible and stable [3]. Methylene blue is a water-soluble cationic dye used in many industrial activities. It is more toxic and causes various diseases such as allergic dermatitis, skin irritation, dysfunction of many organs of human body etc. [4]. Since the harmful impacts of methylene blue dye on exposure of such water, it is necessary to treat waste water before disposal. There are currently numerous treatment processes for effluent discharged from industrial processes containing dyes such as, biodegradation, chemical oxidation, foam flotation, electrolysis, adsorption, electro-coagulation and photocatalysis [5-11]. Most of the conventional methods for the treatment of coloured waste water are expensive and produce large amount of sludge at the end of the process. Among the many methods, adsorption is known to be a promising technique, since it is effective in terms of decolorisation process, simplicity of design, the ease of operation and comparable low cost of application.

Commercially available activated carbon used as an adsorbent material leads to many applications, but its precursor coal is an expensive and non-renewable has restricts its use [12]. Therefore, researchers are finding alternative to commercially activated carbon. An ideal adsorbent must have adsorption efficiency, be relatively cheap and abundant.

In compared to activated carbon, biochar has advantages of large porosity, high surface area, and rich surface functional groups [13]. Also, it has a wide range of sources such as industrial waste, agricultural by-products, livestock manure, sludge etc [14-18]. Some studies have concentrated on the use of animal waste products as a low-cost, readily available adsorbent. Many animal wastes have been studied as possible adsorbents for pollutants removal includes fish bones, pig bones, egg shells, crab shells, and poultry litter etc. [19-23]. As per available reports, one of the fastest growing global industries is dairy farming. According to Ananno et al., the world's cattle population reached 987.51 million in 2020 with estimated global dairy market value is 673.8 billion dollars [24]. This market value is predicted to surpass one trillion dollars by 2024. The large amount of dung produced due to growing population of cattle leads to unavoidable waste management issues. The constituents of cow dung are 12.5% CaO, 0.9% MgO, 0.3% $CaSO_4$, 20% $Al_2O_3$, 20% FeO, and 61% $SiO_2$ [25]. As it contains high percentage of silica, it accounts for its high affinity for metal ions. Thus, it can be used as an adsorbent with great adsorbent potential for pollutant removal from wastewater [25]. There are lots of studies available on modified cow dung adsorbent for pollutant removal [26-30]. The reported studies didn't cover the entire spectrum of pollutants that have been mitigated from aqueous solutions using cow dung-based adsorbents as well as it is required an explanation on the mechanism of adsorption process. In view of this, the goals of the present work are to discuss the proper mechanism of adsorption process and to utilize unmodified cow dung as an effective adsorbent for cost effectiveness.

As animal wastes are much better adsorbents in terms of cost-effective and their zero regeneration process factors. The present research aims to report the efficiency of utilized cow-dung based adsorbents for the removal of methylene blue dye from aqueous media. This work was also attempted to explain the mechanism of adsorption process based on Freundlich, Langmuir and Temkin adsorption isotherms.

## Methodology

In the current study cow dung based low-cost adsorbent is used to remove methylene blue dye from aqueous media. The cow dung cakes were obtained from the nearby places in Baramati city District Pune and were sun dried to remove the entire moisture content. The cow dung cakes were crushed and oven dried at 100 °C for 24 h to ensure drying, then again crushed to convert into powder form. It is then sieved through a 200-mesh sieve to obtain fine particles with a larger surface area. To increase the number of active sites for the adsorption process, the cow dung powder was oven heated for 2 h before it is used as an adsorbent.

Methylene blue dye used as adsorbate was purchased from Research-Lab Fine Chem Industries, Mumbai, India. 0.5 g of dye was dissolved in 500 mL of deionized water to prepare the stock solution of dye (1 g·L$^{-1}$). The dye stock solution was diluted to the required initial dye concentrations, such as 10, 20, 30, 40 and 50 mg·L$^{-1}$. Also, the dye stock solution was diluted to lower concentration and measured it absorption to plot the standard calibration curve.

Adsorption equilibrium studies were performed in batch experiments to investigate adsorption of methylene blue on cow dung-based adsorbent. 0.1g of adsorbent with 50 ml of methylene blue dye in aqueous solution of varying concentrations viz. 10, 20 30, 40 and 50 mg·L$^{-1}$ in 100 ml flasks were shaken at 200 rpm, at room temperature for contact time of 30 min. After adsorption, the adsorbent and supernatant will be subjected centrifugal separation at 4000 rpm for 10 min. Samples were assessed for initial and residual methylene blue dye concentration using UV-Visible Spectrophotometer (UV-1800, Shimadzu) at wavelength 664 nm.

The standard calibration method was adopted by running a series of standard solutions of the dye. The adsorption efficiency was estimated for the various runs performed using batch experiment. To obtain the percentage of the dye that has been removed, following equation was used.

$$\% \, Removal = \frac{C_0 - C_t}{C_0} \times 100 \qquad \text{----(I)}$$

Where, $C_0$ represents the initial concentration in mg·L$^{-1}$ and $C_t$ represents the concentration in mg·L$^{-1}$ remaining in the solution after time t. The equilibrium adsorption capacity $q_e$ (mg·g$^{-1}$) was calculated by the following formula.

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad \text{---(II)}$$

$C_0$ and $C_e$ (mg·L$^{-1}$) are the liquid phase concentrations of methylene blue dye at the initial time and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of the dry adsorbent (g).

## Result and Discussion

### A. Characterization Methylene blue dye

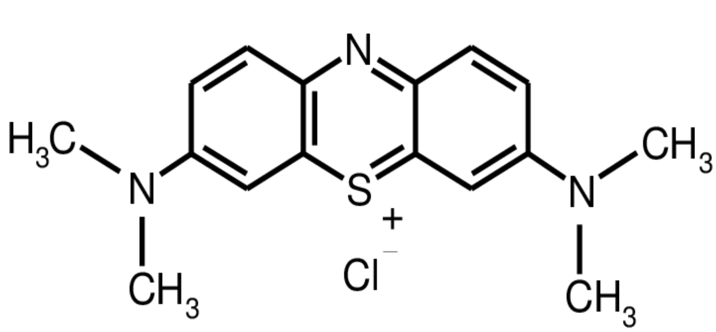
Methylene blue is a dark green crystalline powder at room temperature and gives deep blue shade in aqueous solution. It is an odorless cationic dye and heterocyclic aromatic compound with chemical formula $C_{16}H_{18}ClN_3S$. The complex structure of methylene blue is shown in figure (Fig. 1).

For the confirmation of assay methylene blue dye the UV-Visible spectrum of diluted dye solution from the stock was recorded. From the spectrum, (see Fig. 2.) of a dye solution having concentration 5 mg·L$^{-1}$, the observed absorption maximum at 664 nm ($\lambda_{max}$). It is clear that the adsorbate methylene blue dye in aqueous solution is pure and stable.

After adsorption of methylene blue dye by adsorbent, its concentration were decreased, thus the standard calibration curve were determined at lower concentration. The dye stock solution was diluted to lower concentration (5-20 mg·L$^{-1}$) and measured it absorption to plot the standard calibration curve. The standard curve (Fig. 3) suggests linearity in measurement of absorption as well as dilution made during the experimentation ($R^2$ around 0.998).

### B. Contact time and concentration of adsorbate

50 ml of 20 mg·L$^{-1}$ adsorbate solution was taken in 100 ml conical flask, and 0.1g of adsorbent is added. The absorbance was measured at wavelength $\lambda_{max}$ (664 nm) at different time intervals and the study suggest that 30 minutes are sufficient to achieve the equilibrium between adsorbed and unadsorbed dye concentrations. In the adsorption study it is observed that under experimental conditions, 0.1 g adsorbent is sufficient to remove maximum dye concentrations.



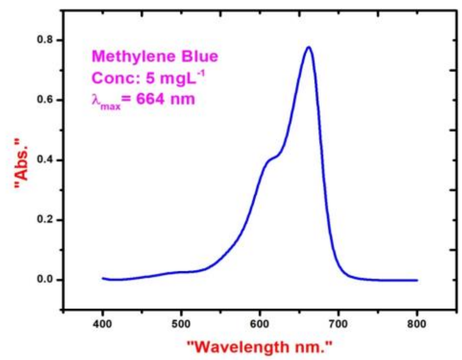
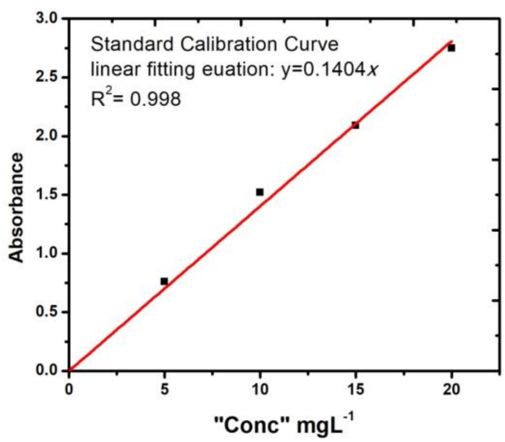



Fig.1 Fig.2

Fig.1: Structure of methylene blue cationic dye Fig. 2: UV-Visible spectrum of methylene blue dye solution (5 mg·L$^{-1}$)



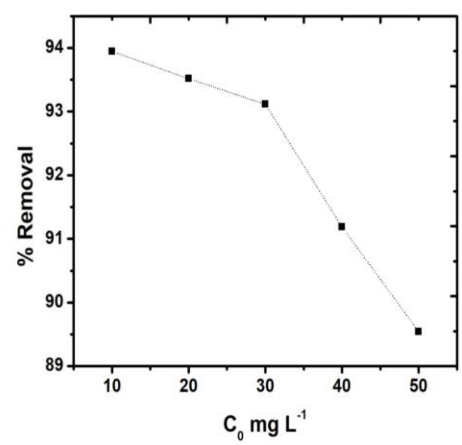




Fig. 3 Fig 4

Fig. 3: Standard calibration curve for methylene blue dye solutions (5-20 mg·L$^{-1}$). Fig. 4: % removal of methylene blue dye against initial concentration (10-50 mg·L$^{-1}$).

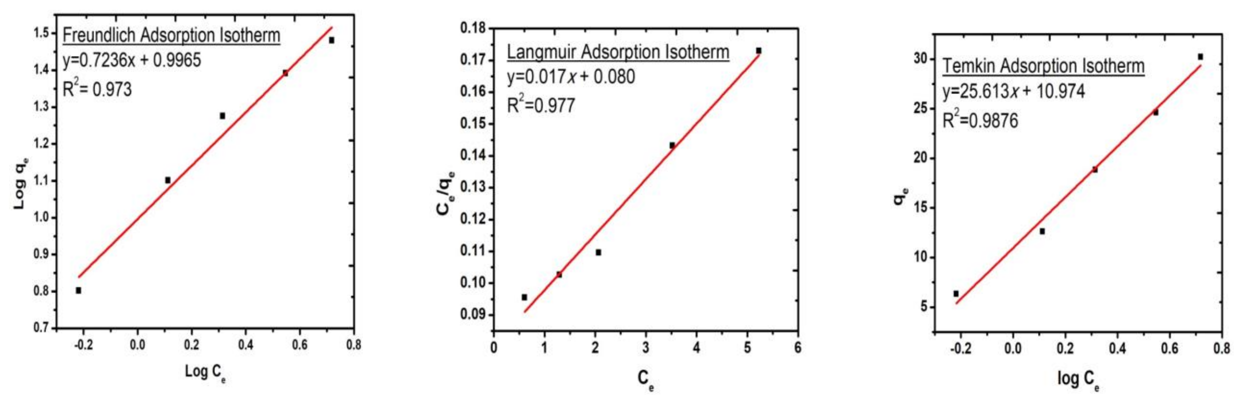



Fig.5: a) Freundlich adsorption isotherm, b) Langmuir adsorption isotherm, c) Temkin adsorption isotherm, for adsorption of methylene blue dye in aqueous solution onto the cow dung-based adsorbent

**Table 1: Isotherm constant parameters and correlation coefficients calculated for removal of methylene blue by cow dung-based adsorbent.**

| Isotherm | Parameter | Value |
|---|---|---|
| Freundlich adsorption isotherm | $K_F$ | 2.709 |
| | n | 1.382 |
| | $R^2$ | 0.973 |
| Langmuir adsorption isotherm | $K_L$ | 0.212 |
| | $q_m$ | 58.824 |
| | $R^2$ | 0.977 |
| Temkin adsorption isotherm | $K_T$ | 1.534 |
| | B | 25.613 |
| | $R^2$ | 0.987 |

### C. Adsorption efficiency

To know the adsorption efficiency of methylene blue dye on cow dung adsorbent, the test samples were taken in which the concentration of dyes were 10, 20, 30, 40 and 50 mg·L$^{-1}$ with 0.1 g adsorbent each flask at a constant temperature. The absorption readings were taken after the equilibrium time. The effect of initial concentration of methylene blue dyes on its adsorption from the aqueous solution is given in Fig. 4. On changing the initial concentration from 10 to 50 mg·L$^{-1}$, showing that with increase in the initial concentration of methylene blue dye, the amount of it removed decreases under experimental conditions, while the % removal of methylene blue dye remains around 90 %.

### D. Adsorption Equilibrium Study

Adsorption equilibrium studies are often used to illustrate adsorbate-adsorbent interactions during adsorption and suggest the mechanism of process. Adsorption equilibrium data are expressed as isotherms. It offers the definite solute distribution between onto the adsorbent and those in the bulk fluid phase at a given temperature. Equilibrium data derived from the various isotherm models provide important insights on adsorption studies. In the present work, Freundlich, Langmuir and Temkin isotherms model were employed to explore the adsorption behavior.

The Freundlich adsorption isotherm is an empirical equation which is functional to adsorption of particles on heterogeneous surfaces of adsorbent. The isotherms work on the assumption that adsorption energy decreases exponentially as the adsorption takes place on adsorbent. The linearized equation of the Freundlich isotherm is:

$$ln(q_e) = \frac{1}{n} ln(C_e) + \ln (K_F) \qquad \text{---(III)}$$

here, $K_F$ is the Freundlich constant (L mg$^{-1}$) and n is the adsorption intensity.

The Langmuir adsorption isotherm assumes a uniform surface of adsorbent with a homogenous distribution of solutes on the adsorbent surface through negligible lateral interactions. Thus, it describes monolayer adsorption due to the presence of specific homogenous sites within the adsorbent. The monolayer adsorption is surface area dependent and has a finite maximum at equilibrium, where, a point of saturation is achieved. After formation of monolayer there is no further adsorption will take place. The mathematical linearized equation to describe the Langmuir adsorption isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \text{---(IV)}$$

here, $q_m$ is maximum adsorption capacity (mg g$^{-1}$) and $K_L$ is the Langmuir isotherm constant (L mg$^{-1}$).

The Temkin adsorption isotherm elucidates the heat of adsorption and adsorbent-adsorbate interactions. Temkin isotherm works on the assumption that the adsorption is mediated by a uniform distribution of binding energies until a maximum binding energy is attained. Also it assumes the heat of adsorption of all the particles in the layer reduces linearly with coverage due to adsorbent-adsorbate interactions. The linearized form of the Temkin adsorption isotherm is:

$$q_e = \frac{RT}{b_T}\ln(K_T) + \frac{RT}{b_T}\ln(C_e) \qquad \text{---(V)}$$

$$and \qquad B = \frac{RT}{b_T}$$

here, $K_T$ is the equilibrium binding constant (L $mg^{-1}$); $b_T$ is the Temkin isotherm constant; T is the absolute temperature (K) and R denotes the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$). Again, B represents the Temkin constant corresponding to the heat of adsorption J $mol^{-1}$).

The adsorption isotherm plots for Freundlich, Langmuir and Temkin isotherms for adsorption of different methylene blue dye concentrations on cow dung-based adsorbent are given in Fig. 5 (5a,5b, and 5c). The fitting parameters of the adsorption isotherm and the correlation coefficients of the experimental data are given in Table 1.

The isotherm data presented in linearized plots and Table 1 showed that a given adsorbent type fulfilled the assumptions of more than one isotherm model. Adsorption parameters estimated from Freundlich, Langmuir and Temkin isotherms to explain the mechanisms of the adsorption process. Based on the correlation coefficient values, cow dung-based adsorbent was best fitted to Temkin adsorption model for removal of methylene blue dye in aqueous solution. From these observations, we proposed that the adsorption in cow dung-based adsorbent takes place due to the adsorbent - adsorbate interactions with distribution a maximum binding energy and the heat of adsorption reduces linearly with coverage in the layer.

## Conclusions

The cow dung-based adsorbent is a low-cost, effective adsorbent for the removal of cationic dye methylene blue from aqueous solutions. The adsorbent had functional adsorption for dye and displayed significant adsorption as the initial dye concentration increased. For the adsorption studies, batch experiments were conducted and showed that the adsorption of methylene blue is depend on contact time, initial concentration of adsorbate and adsorbent dose. The adsorption equilibrium studies were explained based on Freundlich, Langmuir and Temkin isotherms. The adsorption process based on the correlation coefficient values suggest that cow dung adsorbents are best fitted into Temkin isotherm. Thus it deduced that electrostatic interaction is an important mechanism for the adsorption of methylene blue on cow dung based adsorbent. For clear explanations and to overcome the increasing concern of colour effluents, further extended studies are required. Our obtained results from adsorption studies conclude that animal waste cow dung-based adsorbent is an interesting low cost and readily available candidate for the removal of methylene blue from aqueous solutions.

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**Conflicts of interest:** The authors stated that no conflicts of interest.

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