Evaluation of sieved biomass of *Cicer arietinum* (horse bean) for removal of methylene blue: batch study

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**Abstract**

Adsorption of methylene blue by the sieved biomass of *Cicer arietinum* is conducted in batch mode. The effect of different parameters such as contact time, sorbent dose, pH, and temperature has been studied. The adsorption rises substantially as pH is increased from 2 to 4, and then with the increase to pH 10, there is slight decrease in the percentage of adsorption. This may be due to the electrostatic forces of attraction between [MB]^+ cations and the OH^- ions which are greater at low pH in the solution. In the highly acidic medium, there are an ample number of H^+ ions. These can neutralize the negative sites on biosorbent surfaces, leading to a lesser adsorption. The Langmuir model fit and Hall separation values indicate favorable adsorption. Thermodynamic parameters via KD and ΔG have also been calculated: the ΔG value at 15°C is −943 J/mole, while at 45°C, the value of ΔG is −4,010 J/mole. At the higher concentration, KD values decrease and the ΔG values become positive in the same temperature range, indicating the spontaneity of the process. Kinetics of biosorption results shows that the sorption process is well explained by a pseudo-second-order model with determination coefficients of 0.4841 to 0.9962 for S-II under all experimental conditions. The sorption mechanism was determined by the Weber and Morris intraparticle diffusion model. For the initial concentration of 79.9 mg/L and material dose of 500 mg/L, the value of Kid and the intercept was found to be 4.359 and 22.557, respectively, indicating that the foundry layer is sufficiently thick. The low-cost, easily available agro-waste of *C. arietinum* was found to be a good adsorbent for the methylene blue dye.

**Keywords:** Methylene blue; Biosobent; Adsorbent; Adsorption; Sieved biomass S-II

**Introduction**

Increasing water pollution is becoming a matter of great concern; dyes may also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea, if inhaled. They are likely to cause irritation to the skin and are highly dangerous to biota. Dyes may also be problematic if they are broken down anaerobically in the sediments, as toxic amines are often produced due to incomplete degradation by bacteria (Weber and Wolfe 1987). Synthetic dyes have a complex aromatic structure which provides them physiochemical, thermal, biological, and optical stability (Mckay 1982). Literature also reports the removal of dyes such as malachite green (Mall and Upadhyaya 1998; Deshmukh et al. 2004), crystal violet, methyl red, eriochrome black T, deorlone, saffranine red (McKay and Al-Durl 1989), acid orange-7, acid red-88, acid blue 113, and methyl violet by different available adsorbents, such as silica and alumina (Singh and Prasad 1975). However, these adsorbents do not prove to be cost effective. Synthetic dyes are widely used in many industries including textile dyeing and paper printing. Color- and dye-bearing wastewater discharged into water streams not only contributes negatively to aesthetic value but also causes considerable resistance to biodegradation and may upset aquatic life (Mishra and Tripathy 1993). Such colored wastewater is unfit for recycling without proper treatment. Some of the dyes or their metabolites are not only toxic or mutagenic but also carcinogenic (Sivaraj et al. 2001). Basic dyes are the brightest class of soluble dyes used by the textile industry (Kapoor and Kalani 1984; Reid 1996). Most dyestuffs are designed to be resistant to environmental conditions...
such as light, heat, and microbial attack and also to oxidizing agents (Pagga and Taeger 1994), making the biodegradation of dyes a very slow process (O’Mahony et al. 2002). Adsorbents prepared from sugarcane bagasse, an agro-industrial waste, have been successfully used to remove the dye methyl red from an aqueous solution in a batch reactor. These adsorbents have been investigated by Saiful Azhar et al. (2005) by pretreating sugarcane bagasse with formaldehyde and sulfuric acid. Sugarcane bagasse is a cheap and abundantly available biomass, and adsorption is an ecofriendly and economically feasible dye removal technique (Churchley et al. 2000). The conventional technologies used for the removal of dye-stuffs include chemical coagulation/flocculation, ozonation, membrane filtration, anaerobic degradation, etc. These methods suffer from having low efficiency for reactive dyes and are also very expensive. These processes are therefore not very effective in treating wastewater containing dyes. They are also not cost effective especially for developing countries (Bousher et al. 1997). The adsorption of dyes on these materials is reported to be fast and is completed within a short interval of time (Ram and Prasad 1985; Giles and D’silva 1996; Calbraith et al. 1958). The US Environmental Protection Agency (USEPA) has classified textile wastes into four groups: (1) dispersible, (2) hard-to-treat, (3) high-volume, and (4) hazardous and toxic wastes (Arami et al. 2005). The batch experiments have been carried out by Raghuvanshi et al. (2004) to study the kinetics of adsorption of methylene blue dye on bagasse with two different forms, like raw and chemically activated forms. Spectrometric studies have been accomplished by Rasheed Khan et al. (2005) for adsorption of dye methylene blue from an aqueous solution on the surface of sheep wool and cotton fiber under optimal conditions of temperature, concentration, pH, stay time duration, and amount of adsorbent. From the related literature, several biological materials have been reported as dye bioadsorbents, including banana and cotton fiber (Dash Deepak 1998), orange fruit peels (Annadurai et al. 2002), and wheat bran (Hamdaoui and Chiha 2007; Ghosh and Bhattacharyya 2002; Sharma et al. 2007). A wide range of waste materials can be used as raw materials for the new and novel adsorbents. Unconventional adsorbents like fly ash, bagasse, peat, lignite, wood, and saw dust which fall into the above categories have therefore attracted the attention of several investigators. Adsorption characteristics of these materials have been widely investigated for removal of organic matter, such as organic acid dyes (Arami et al. 2006), phenol, refractory organic, and heavy metals. The present work deals with the study of the adsorption mechanism of methylene blue dye using an easily available and ample amount of a low-cost sieved agro-waste of *Cicer arientinum*.

**Methods**

**Sorbate and chemicals**

The solutions of the dye methylene blue (3, 9 bis-diamino phenathionium chloride) sorbate having a molecular formula $C_{16}H_{18}N_3SCl$ were prepared by dissolving appropriate amounts of dry powdered dyestuff in bidistilled water. Concentrations of the solutions used for this study were 0.799, 7.99, 39.9, and 79.99 mg/L (all chemicals used are from Merck Chem., Whitehouse Station, NJ, USA).

**Preparation of sorbent**

Stalks of the agro-waste of *C. arientinum* were collected, cleaned, and shade dried. They were then crushed, powdered, and passed through a 0.63-mm mesh to get uniform-sized particles of sorbent. They were dried at 110°C in the oven for 3 h and stored in vacuum desiccators before use.

**Sorption kinetics**

There were three sets of experiments, and each set includes 50 mg of sorbent which was placed in different conical flasks. To each of these flasks, 25 mL of dye solution of initial concentration ($C_0 = 0.799$ mg/L) was added. The volume was made up to 100 mL by adding distilled water.
The flasks were protected from sunlight and stirred using a magnetic stirrer with a constant speed of 400 rpm for a period of 2, 4, 6, 8, 10, 12, 14, 30, and 60 min, respectively, and filtered through a Whatmann filter paper. The absorbance of the filtrate was measured using a Systronics-112 photoelectric colorimeter (Systronics, Ahmedabad, India) using a filter with a wavelength of 640 nm. The same procedure mentioned above was used to study the effect of different variables mentioned in this work. The dye uptake capacity for the adsorbate was calculated using a simple concentration method. Uptake capacity was calculated from the mass balance as follows:

\[
q = \frac{(Co - Ct) \times V}{100}
\]

Where \(q\) is the quantity of sorbate (dye or metal) uptake by the biomass, and \(Co\) and \(Ct\) are the initial and final concentrations, respectively. \(V\) is the volume of solution in milliliters and \(W\) is the dry weight of the biomass added. Calibration and actual experiments were carried out in triplicate, and mean values are presented.

**Sorption kinetic models**

**Percentage removal analysis of sorption data**

The removal percentage is calculated by the equation

\[
PR (\%) = \left(1 - \frac{Ce}{Co}\right) \times 100
\]

Where \(PR (\%)\) is the removal percentage of the dye or metal ion from the static system after agitation, \(Co\) is the initial metal ion concentration, \(Ct\) is with a fixed dosage of adsorbent, and \(Ce\) is the sorbate concentration at the experimental equilibrium stage.
Langmuir isotherm model

Langmuir isotherm was applied for adsorption equilibrium data. The Langmuir isotherm is based on the following assumptions:

- Adsorbate/metal ions are chemically adsorbed at a fixed number of well-defined sites.
- Each site can hold only one ion.
- All sites are energetically equivalent, and there is no interaction between adsorbed ions. When the initial sorbate concentration increases, adsorption increases while the binding sites are not saturated. The unmodified Langmuir equation is as follows:

\[
Q_e = \frac{ab}{1 + bC_e},
\]

where \(a\) is the maximum adsorption capacity (mg/g) and \(b\) is the Langmuir isotherm parameter related to the energy of adsorption (1/mg).

Freundlich isotherm model

The Freundlich equation is used for the heterogeneous surface energy term. The Freundlich isotherm can also be used to explain the adsorption phenomenon as follows:

\[
Q_e = K_f C_e^{1/n},
\]

The linearized Freundlich model isotherm is represented by the equation

\[
\log 10Q_e = \log 10 K_f + \frac{1}{n} \log 10 C_e,
\]

where \(K_f\) and \(n\) are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto carbon, respectively.

Adsorption thermodynamic equation

The value of the thermodynamic parameter free energy \(\Delta G^°\) was calculated using the following thermodynamic equation (Sarin and Pant 2006):

\[
\Delta G^° = -RT \ln K,
\]

where \(\Delta G^°\) is the change in free energy (KJ/mol), \(T\) is the absolute temperature (K), \(R\) (universal gas constant) is equal to 8.314 J/mole-K, and \(K\) is the equilibrium constant at temperature \(T\). The equilibrium constant \(K\) can be calculated from

Figure 4: Plot of \(x/m\) vs. \(T\) for S-II with varying initial concentrations.

Figure 5: Plots of percentage of adsorption vs. \(T\) for S-II with varying temperatures. \(C_o = 0.799\) and 79.9 mg/L.
$K = \frac{qe}{Ce}.$

**Kinetic models**

Kinetics of methylene blue (MB) adsorption on the sieved biomass of *C. arientinum* can be modeled by the pseudo-first-order Lagergren equation and pseudo-second-order model. The rate constant of adsorption from the first-order rate expression is

$$\log (qe-qt) = \log qe - Kt = 2.303t,$$

where $qe$ and $qt$ are the amount of dye adsorbed (mg/g) at equilibrium, and $Kt$ is the rate constant. The second-order kinetics model is expressed as

$$t/q = \frac{1}{K_2 qe^2} + \frac{t}{qe}.$$

The initial adsorption rate (mg/g) can be defined as $n = k_2 qe^2$.

The initial adsorption rate (h), equilibrium adsorption capacity ($qe$), and second-order rate constant $K_2$ (g/mg min) are determined experimentally from the slope and intercept of the plot.

**Intraparticle diffusion study**

Adsorption by porous particles is a process which involves a number of steps. The most common empirical function which explains adsorption is that the uptake varies almost proportionally with $t^{1/2}$ rather than contact time.

According to the equation, the plot of $qt$ vs. $t^{1/2}$ should be a straight line passing through the origin, when the intraparticle diffusion is the rate-controlling step. If the plot of $qt$ vs. $t^{1/2}$ is nonlinear, it indicates that the adsorption is not governed by a single mechanism.

**Result and discussion**

**Characterization of biosorbents**

The physical parameters like bulk density (g/cc), moisture content, volatile matter, and ash content are 0.58%, 6.8%, 17.5%, and 8.5%, respectively. The IR spectrum of the sieved biomass of *C. arientinum* shows absorption peaks at 3,342 cm$^{-1}$ for broad -OH, 2,930 cm$^{-1}$ for -NH, and 1,735 cm$^{-1}$ for COOH.

**Effect of time**

The percentage of adsorption vs. time indicates that the adsorption is initially very rapid and that the rate then slowed down (Figure 1 for [MB]$^+$). The percentage of removal increases with time; equilibrium is attained within 30 min in all cases. For a sorbent dose of 50 mg/L, the adsorption was 81.45%, while at a sorbent dose of 500 mg/L, the percentage of removal was 90.69%. This can be understood easily from the fact that with increasing sorbent dose, more number of sites were available for adsorption of the dye molecule, and also, a larger surface area causes fast sorption.

**Effect of sorbent dose**

The plots were showing rapid adsorption in the initial stage and a decreased uptake later on (Figure 2). The experiments revealed that for a given initial concentration, e.g., 79.9 mg/L, the percentage of removal increases as

| n | Table 2 Thermodynamic parameter and variation in ΔG |
|---|---|---|---|
| 0.799 | 2.76 | $-2,517.18$ |
| 7.99 | 5.36 | $-4,247.0$ |
| 39.9 | 5.6 | $-4,407.7$ |
| 79.9 | 0.77 | $+628$ |
dose was increased. However, adsorption capacity does not increase with increase in sorbent dose. The $x/m$ value decreases as the dose is increased from 50 to 500 mg/L. As the dose increases, the amount of dye adsorbed per unit gram of sorbent decreases. A rapid adsorption is observed at the initial stage due to strong attractive forces between the dye molecules and sorbent. The time required for attaining equilibrium is also very short, probably due to the fast diffusion of the dye into the intraparticle matrix from the solution.

Effect of pH

The effect of pH on adsorption of MB was studied on the material S-II in the pH range of 2 to 10 (Figure 3). As seen in the plots, in the initial stages, the percentage of adsorption rises substantially as pH is increased from 2 to 4, but as pH is increased from 4 to 10, there is a slight decrease in the percentage of adsorption. This may be due to the electrostatic forces of attraction between [MB]$^+$ cations and the OH$^-$ ions in the solution. In the highly acidic medium, there are an ample number of H$^+$ ions. These can neutralize the negative sites on the biosorbent surface, leading to a lesser adsorption of the [MB]$^+$. As pH increases from 4 to 6, this interaction decreases and more sites are available for adsorption of [MB]$^+$, leading to an increase in the percentage of adsorption. In the basic medium, although more sites are available for adsorption, the electrostatic interactions between the [MB]$^+$ and OH$^-$ in the solution seem to be operative, which holds the [MB]$^+$ in the solution, thus leading to the decrease in the percentage of adsorption above pH 6.

Effect of initial concentration

Initial concentration affects the uptake capacity of the biosorbent to a large extent (Figure 4). For a fixed material dose (50 mg/100 mL), the adsorption increases from 17 to 63.08 for initial concentrations of 0.799, 7.99, 39.9, and 79.9 mg/L of the dye. The adsorption capacity is observed to increases from 1.02 to 6.125, indicating that a dynamic equilibrium exists. A given sorbent mass has a fixed number of adsorption sites. As the concentration of the sorbent increases, at a given time instance, there are more number of sorbate molecules interacting with the sorbent, leading to an increase in the percentage of removal.

Effect of temperature

As temperature increases, an increase is observed in $x/m$ for all values of Co. The curves indicate that as temperature increases, the sorption capacities also increase. The equilibrium sorption capacities increase from 11.7 to 12.1 mg/g (Co = 0.799 mg/L) (Figure 5) and from 12.78 to 13.6 mg/g (Co = 7.99 mg/L). The increase in sorption capacities with temperature indicates that with increasing temperature, mobility of the [MB]$^+$ ions increases. It can also be said that with rise in temperature, the interactions between the dye molecules and the sorbent surface become more effective; the increase in the value of $x/m$ with temperature also indicates the sorption process to be endothermic.

Adsorption isotherms

Although the plots of $Ce/x/m$ vs. $Ce$ were straight lines, the values of the Langmuir constant were negative (Figure 6). The data were fitted in the Freundlich model, and the following values of slope and intercept were observed (Figure 7).

An increase in value of the adsorption capacity Kf and intensity of the adsorption $1/n$ reveals the increase in
affinity of methylene blue towards the biosorbent with a rise in temperature (Table 1). The values of $1/n$ less than unity indicate favorable adsorption and formation of stronger bonds between the adsorbent and adsorbate. The values of $a$ and $b$ were found to be 8.66 and 0.09, respectively, while the Hall separation factor is 0.114.

There is an increase in the values of $K_D$ and $\Delta G$ with increase in temperature, indicating the spontaneity of the adsorption process (Table 2). The $\Delta G$ values are found to be negative for initial concentrations at 25°C, and for $C_0 = 79.9$ mg/L, the values of $\Delta G$ become positive, indicating nonspontaneity of the adsorption at higher concentration. The $\Delta G$ values for initial concentrations of 0.799, 7.99, and 39.9 mg/L become more negative with increasing temperature. At an initial concentration of 0.799 mg/L, the $\Delta G$ value which is also temperature dependent at 15°C is $-943$ J/mole, while at 45°C, the value of $\Delta G$ is $-4,010$ J/mole. At the higher concentration, $K_D$ values decrease and the $\Delta G$ values become positive in the same temperature range.

**Kinetic modeling**

The Lagergren first-order model indicated that the plots of the log $q_e$-qt vs. time are expected to be linear. The plots of our data (Figure 8) indicate nonlinearity for all temperatures and initial concentrations at which the studies were carried out; the coefficients of the determinant are also seen to vary in the range of 0.4841 to 0.9962. These results indicate the non-applicability of the model. The other commonly used model is the pseudo-second-order model proposed by McKay and Ho which is expressed as $t/q = 1/k_2 q_e^2 + t/q_e$. The plots of the $t/qt$ vs. $t$ were found to be linear and straight lines as seen in Figure 9. The calculated coefficients are closer to unity for second-order kinetics. Therefore, the adsorption kinetics could be well approximated more favorably by this model. The values of the pseudo-second-order rate constant $K_2$ and the correlation coefficient are given in Table 3.

**Intraparticle diffusion studies**

The intraparticle diffusion studies indicated that the process takes place in three steps (Figure 10). The initial part of the curve is attributed to the mass transfer effect, while the final linear portions are attributed to intraparticle diffusion. The $K_d$ intraparticle diffusion constant is calculated from the slope of the linear portion, while the value of the intercept gives an idea about the thickness of the boundary layer. For the initial concentration of 79.9 mg/L and material dose of 500 mg/L, the value of $K_d$ was found to be 4.359. The value of the intercept is 22.557, and this indicates that the foundry layer is sufficiently thick.

**Conclusions**

For all concentrations, the sorption equilibrium is attained within 30 min. The adsorption is initially very rapid, and the rate then slows down. For an initial concentration ($C_0 = 7.99$ mg/mL), the percentage of adsorption increased as the sorbent dose was increased. For a sorbent dose of 500 mg/L, adsorption was 81.45%; for a sorbent dose of 5 g/L, the percentage of adsorption was 90.61% for the biosorbent. A decrease in adsorption capacity from 58.7 to 7.733 mg/g is observed, as the sorbent dose changes from 50 to 500 mg/L for the biosorbent. The amount adsorbed is maximum at pH 4. A slight decrease is observed when the pH is raised from 4 to 6, in the range of 6 to 10. Removal of the dye is insignificant. The pH of the aqueous solution has an effect on both the binding sites of the sorbents and the sorbate. As temperature increases, the sorption capacities also increase. The value of $K_d$ increases with increase in temperature. The $\Delta G$ values at the different temperatures studied have negative values, indicating spontaneity of the process. Kinetic modeling indicates that the sorption process follows a pseudo-second order, having low $K$ values at a high concentration of 79.9 mg/L and a high $K$ value for a lower concentration of 0.79 mg/L. The values of $K_f$ range between 4.4 and 7.9, and the values of $1/n$ are less than unity, indicating good intensity of adsorption for temperatures of 15°C,

![Figure 10 Plot of Q vs. $t^{1/2}$ for S-II with concentrations. Co = 0.799 mg/L and Co = 79.9 mg/L.](image-url)

**Table 3 Pseudo-second-order rate constant $K_2$ and the correlation coefficients on S-II**

| Initial concentration (mg/L) | $K_2$  | $R^2$ |
|------------------------------|--------|-------|
| 0.799                       | 0.9427 | 0.9972 |
| 7.99                        | 0.0726 | 0.998  |
| 39.9                        | 0.0183 | 0.961  |
| 79.9                        | 0.014  | 0.9692 |
25°C, 35°C, and 45°C. The Langmuir model fit and Hall separation values indicate favorable adsorption. The intraparticle diffusion studies indicate that intraparticle diffusion, mass transfer, etc. are the rate-determining step of adsorption.

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