Determination of equilibrium, kinetic and thermodynamic parameters for the adsorption of Brilliant Green dye from aqueous solutions onto eggshell powder

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The removal of the Brilliant Green (BG) dye using hen eggshell powder (abundantly available and a total waste material) has been explored. Adsorption studies for the dye removal by eggshell powder has been carried out under varying experimental conditions of adsorbent dose, temperature, contact time, initial dye concentration and pH. The equilibrium data has been studied using the Langmuir isotherm equation. Monolayer adsorption capacity of hen eggshell powder for BG dye is found to be 44.7 mg/g, 34.23 mg/g and 30.23 mg/g at temperatures 303, 313 and 323 K respectively. The kinetic study on BG suggests that the adsorption follows the pseudo-second order kinetics. Adsorption follows both surface adsorption and intra-particle diffusion mechanisms. The Arrhenius energy of activation observed from the experimental data is found to be -15.88 kJ/mol which suggests that the energy barriers are absent in the adsorption process and the reaction is exothermic. The thermodynamic study on BG reveals that the reaction is spontaneous, exothermic and proceeds with decreased randomness at the solid-solution interface as the entropy change (-19.08 J/mol/K) is negative.

Keywords: Brilliant Green dye, Hen eggshell powder, Isotherm, Sorption, Thermodynamics

Presently, it is estimated that about 10,000 of different commercial dyes and pigments exist and over $7 \times 10^5$ tonnes are produced annually worldwide. Dyes have long been used in dyeing paper, pulp, textiles, plastics, leather, cosmetics and food industries. Coloured stuff discharged from these industries poses certain hazards and environmental problems as they are generally believed to be toxic and carcinogenic or prepared from other known carcinogens. These coloured compounds are not only aesthetically displeasing but also inhibit sunlight penetration into the water thus preventing photosynthesis and affect aquatic ecosystems. Unless properly collected, treated and disposed of, such type of wastewater create serious water pollution problems.

Brilliant Green (BG) (Fig. 1) is a cationic and triarylmethane dye of the malachite green series. It is chemically known as 4,4-bisdiethylaminotriphenylmethylsulfate. BG is highly resistant to microbial degradation. BG dye, besides being a compound of biological interest, has a major use in the dye industry for dyeing and printing all types of fibres, viz., cotton, wool, silk, etc. BG is harmful if in contact with skin and if swallowed. It is irritating to respiratory system and skin. There is a risk of serious damage to eyes. It is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Inhalation may produce serious health damage and it is also investigated as a mutagen in microorganisms.

In order to achieve a high degree of dye removal from aqueous solution, it is necessary to integrate biological, chemical and physical processes such as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation. Physical adsorption techniques are generally considered as the preferred means for removing and purifying organic substances due to their high efficiency and ability to separate a wide range of...
chemical compounds. The adsorption process provides an attractive alternative treatment, especially when the adsorbent is inexpensive and readily available. Granular activated carbon is the most popular adsorbent and has been used with great success, but is expensive. Consequently, many investigators have studied the feasibility of low cost substances for the removal of Brilliant Green dye such as neem leaf powder, bagasse fly ash, rice husk ash, pine fruit shell, deoiled soya, almond peel, jute sticks and coconut fibre. All avian eggshells share the same mineral component, namely the trigonal phase of calcium carbonate (CaCO₃), known as calcite, which is the more stable polymorph at room temperature.

In this study, an attempt has been made to use an ecofriendly and cost effective adsorbent (hen eggshell powder—a waste material) for the treatment of dye containing aqueous solution.

Experimental Procedure

Eggshells collected from the local poultry chickens were thoroughly cleaned with de-ionized water and dried in a microwave oven for 60 min at 100 °C. It was then cooled and powdered in a mechanical grinder and sieved through 100 µm sieve. The powder was washed with double distilled water three times and dried for 60 min at 100 °C in a microwave oven. The powder was then stored in an air tight container and was used for the study.

The BG dye was obtained from Central Drug House Pvt. Ltd, India and then used without further purification. A stock solution of 1000 mg/L of the BG dye was prepared by dissolving 1g of the dye in double distilled water and making up the volume to 1 L. The stock solution was diluted accordingly to obtain working solutions of desired concentrations.

The batch adsorption experiments were carried out in a mechanical stirrer (REMI 2MLH) at 150 rpm using 100 mL shaking flasks containing 50 mL of dye solutions of 100 mg/L concentration. Influence of each parameter (pH, initial dye concentration, adsorbent dose, temperature and contact time) was evaluated by varying the parameter under evaluation, while all other parameters in the experiment were maintained as constant. After stirring, the solutions were centrifuged to get clear supernatant and the dye concentration in the supernatant was calculated by measuring absorbance at 624.4 nm (λ_max) with a Systronics Spectrophotometer-104. The equilibrium solid phase concentration qₑ (mg/g) was then calculated according to the following equation:

\[ q_e = \frac{(C_i - C_e) \times V}{m} \]  

where \( q_e \) (mg/g) is the amount of dye adsorbed by the biomass; \( C_i \) and \( C_e \) (mg/L), the initial and equilibrium liquid phase concentration of dye; \( V \) (L), the initial volume of dye solution; and \( m \) (g), the weight of the eggshell powder. All the experiments were repeated thrice and the mean values were calculated.

Results and Discussion

Influence of pH

Adsorption of BG onto eggshell is influenced by the pH of the solution. The pH at point zero charge \((pH_{PZC})\) of the hen eggshell powder was determined by the solid addition method. The \( pH_{PZC} \) of hen eggshell powder is found to be 7.2. At \( pH < pH_{PZC} \), the surface becomes positively charged, concentrations of \( H^+ \) remains high and they compete with dye cations for vacant adsorption sites, causing a decrease in dye uptake. At the solution having \( pH > pH_{PZC} \), the adsorbent surface becomes negatively charged and favours uptake of cationic dye due to increased electrostatic force of attraction. The results show that the dye removal increases with increasing initial \( pH \) of the dye solution and maximum removal occurs at \( pH \) 9. Therefore, further experiments were carried out at \( pH \) 9.

Effect of adsorbent dose

The adsorption of the dye on eggshell was studied by varying the eggshell amount from 0.4 g/L to 6 g/L. It is observed that the percentage of adsorption increases as the eggshell dose is increased. This is attributed to the increase in the eggshell surface area and availability of more adsorption sites. At 4 g/L dose, there is almost complete removal (99%) of dye. Thus, 4 g/L is used as an adsorbent dose for all the future experiments.

Effect of contact time

Figure 2 shows that about 80% of the dye removal occurs within the first 15 min and then it gradually...
increases to about 99% in the next 15 min. As maximum adsorption occurs within the first 30 min without further appreciable adsorption thereafter, 30 min has been deemed as the equilibrium time.

Influence of initial dye concentration

The influence of dye concentration on the adsorption of the dye is shown in Fig. 2. When the dye concentration is increased from 100 mg/L to 200 mg/L, the percentage of dye adsorbed decreases from 99% to 92%. The result shows that the % removal depends on the initial dye concentration. In case of low dye concentrations, the ratio of the initial number of moles of the dye ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher dye concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions which depends upon the initial concentration, decreases.

Adsorption isotherm

The Langmuir equation is based on the assumption that maximum sorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following linear equation:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}}bC_e} \quad \ldots (2)
\]

where \(q_{\text{max}}\) is the monolayer adsorption capacity (mg/g); and \(b\), the Langmuir constant (L/mg) related to the free energy of adsorption. When \(1/C_e\) is plotted against \(1/q_e\), a straight line with a slope of \(1/q_{\text{max}}b\) is obtained (Fig. 3), indicating that the adsorption of BG on eggshell follows the Langmuir isotherm in the range 303 - 323 K. The Langmuir constants \(b\) and \(q_{\text{max}}\) are calculated from the plot and their values are listed in Table 1. Monolayer adsorption capacity of hen eggshell powder for BG dye is found to be 44.7 mg/g, 34.23 mg/g and 30.23 mg/g at temperatures 303, 313 and 323 K respectively.

Adsorption kinetics study

In order to understand the process of adsorption, three kinetic models (i) Lagergren’s pseudo-first order model (Eq. 3), (ii) Ho’s pseudo-second order model (Eq. 4) and (iii) Weber and Morris intra-particle diffusion model (Eq. 5) were applied to analyze the experimental data.

(i) The linearized form of pseudo-first order kinetic model can be written as:

\[
\ln (q_e - q_t) = \ln q_e - k_1t \quad \ldots (3)
\]

where \(q_e\) and \(q_t\) are the amount of BG dye adsorbed at equilibrium and at time \(t\) (mg/g) respectively; and \(k_1\) (min\(^{-1}\)), the rate constant of adsorption. The values of \(k_1\) and \(q_{\text{cal}}\) were calculated from the slopes (-\(k_1\)) and intercepts (ln\(q_e\)) of the plots ln (\(q_e - q_t\)) vs \(t\) (Fig. 4),
respectively, and are presented in Table 2. Plots of Eq. 3 show lower correlation coefficient values and the calculated \( q_e \) values of pseudo-first order equation are found to be lower than the experimental one, indicating that pseudo-first order model is not fit to describe kinetic data.

(ii) The pseudo-second order adsorption kinetics\(^{19}\) can be written as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots \quad (4)
\]

where \( k_2 \) is the rate constant of adsorption (g/mg min). The values of \( k_2 \) and \( q_e^{\text{cal}} \) were calculated from the intercepts (1/\( k_2 q_e^2 \)) and slopes (1/\( q_e \)) of the plots \( t/q_t \) vs. \( t \) (Fig. 5), respectively and are presented in Table 2. The correlation coefficients of pseudo-second order models are closer to unity and the calculated \( q_e \) values computed from pseudo-second order equation show good agreement with experimental values, indicating the applicability of pseudo-second order kinetic model for adsorption of BG dye on hen eggshell powder. Results show that the values of rate constant decreases as temperature increase.

(iii) The intra-particle diffusion model is based on the following Morris – Weber equation\(^{20}\) for the rate constant:

\[
q_t = k_i t^{0.5} + C
\]

\[
\ldots \quad (5)
\]

where \( k_i \) is the intra-particle diffusion constant (mg/g min\(^{0.5}\)); \( t \), the time (min); and the intercept \( C \) reflects the boundary layer effect. The values of \( k_i \) were calculated from slopes (\( k_i \)) of the plots \( q_t \) vs. \( t^{0.5} \) (Fig. 6) and presented in Table 2. As shown in Fig. 6, the plot can be approximated to be linear over the range of adsorption but does not pass through the origin. Higher \( C \) value observed at 303 K. Larger the value of \( C \), greater is the contribution of the surface adsorption in the rate-limiting step. Value of \( k_i \) is higher at 323 K due to higher concentration of dye present in solution phase after surface adsorption. This results in an increase of the concentration gradient (driving force), which increase the diffusion rate. Results confirm the presence of both surface adsorption and intra-particle diffusion mechanism during adsorption of dye.

The pseudo-second order rate equation of BG adsorption on eggshell powder is expressed as a function of temperature by Arrhenius equation, as shown below:

\[
\ln k = \ln A – \frac{E_a}{RT}
\]

\[
\ldots \quad (6)
\]
where $E_a$ is the Arrhenius activation energy (kJ/mol); $A$, the Arrhenius factor; $R$, the gas constant; and $T$, the solution temperature. Positive activation energy is the energy that must be overcome for a adsorption to occur\cite{1,2,21,22}. However, negative activation energy indicates the absence of energy barrier to cause the adsorption to occur. The $\ln k$ vs $1/T$ gives a straight line with slope $-E_a/R$ and intercept $\ln A$, as shown in Fig. 7. The value of the specific rate constant ($k$) is $k_1/k_2$, where $k_1$ and $k_2$ are rate constants at temperatures $T_1$ and $T_2$. The Arrhenius activation energy calculated from the slope is found to be -15.88 kJ/mol. The negative value of the activation energy indicates that energy barriers are absent in the reaction process and that the reaction is exothermic. On increasing the temperature there is a reduction in the probability of the colliding molecules capturing one another, and this results in a negative activation energy.

**Thermodynamic study**

Figure 8 shows the effect of different temperatures for BG adsorption on eggshell powder. The removal of BG is decreased from 98 % to 73 % on increasing the temperature from 303 K to 323 K, indicating the process to be exothermic. The thermodynamic parameters for the adsorption of BG by eggshell were observed using the following basic thermodynamic relations\cite{23}:

$$
\Delta G^o = -RT \ln K_c \quad \ldots (7)
$$

$$
\ln K_c = \Delta S^o/R - \Delta H^o/RT \quad \ldots (8)
$$

where $R$ is the universal gas constant, 8.314 J/mol/K; and $T$, the absolute solution temperature (K); and $\Delta H^o$, $\Delta S^o$ & $\Delta G^o$ are the changes in enthalpy (J/mol), entropy (J/mol/K) and Gibb’s free energy (J/mol) respectively. The plots of $\ln K_c$ vs. $1/T$ (Fig. 7) gives the straight line from which $\Delta H^o$ and $\Delta S^o$ are calculated from the slope and intercept of the linearised form. The value of $\Delta G^o$ is -3.31, -1.94 and -0.11 kJ/mol at 303, 313 and 323 K respectively. The negative value of $\Delta G^o$ confirms the spontaneity and feasibility of the adsorption process and the negative value of $\Delta H^o$ (-51.47 kJ/mol) suggests that the adsorption is exothermic in nature. The negative $\Delta S^o$ (-19.08 J/mol/K) interprets the decreased randomness at the solid – solution interface.

**Conclusion**

The study shows that the hen eggshell is an excellent adsorbent for removal of the cationic dye (Brilliant Green) from aqueous solution. The pH 9 and temperature 303 K are found to be optimum for adsorption. Monolayer adsorption capacity is found to be 44.75 mg/g at 303 K. The adsorption equilibrium is reached in 30 min. The adsorption processes follow the pseudo-second order rate kinetics. Both intra-particle diffusion and surface adsorption contribute to the control of the rate of adsorption. The Arrhenius activation energy of -15.88 kJmol$^{-1}$ suggests that energy barriers are absent in the reaction process and that the reaction is exothermic. Negative values of Gibb’s free energy change ($\Delta G^o$) show that the adsorption is feasible and spontaneous and negative values of enthalpy change ($\Delta H^o$) confirm exothermic adsorption.
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References