Chapter – 6

Adsorption of Amaranth Dye onto Alumina Reinforced Polystyrene

6.1. Introduction

The textile industries are major consumers of synthetic dyestuffs and utilize large volumes of water in wet processing operations. Dyes in wastewaters affect the nature of water by inhibiting the sunlight penetration into the stream thereby reducing the photosynthesis reaction [1]. Some synthetic dyes such as azo dyes may be carcinogenic or mutagenic and under anaerobic conditions, can be transformed into aryl amines which are potentially more toxic than the parent compounds [2-3]. Amaranth is an azo dye and its toxicity has been reported for some animals for eg. carcinogenic to rat fetus. The amaranth dye is degraded by intestinal microorganisms in vivo and is possible that the toxic or carcinogenic effects may be due to their degradation products [4].

Numerous advanced technologies such as adsorption, membrane separation, flocculation-coagulation, aerobic or anaerobic treatment have been developed and applied worldwide for the scavenging of dyes [5]. Among these processes, the adsorption is widely applied because of the system flexibility, low cost as well as low energy consumption. A wide variety of porous materials, such as agricultural waste [6], polymers [7-9], carbon materials [10-12], clay minerals [13-16], and other solid materials [5, 17-20] have been investigated as adsorbents for the removal of dyes. In recent years, polymeric composite adsorbents have been increasingly used to remove and recover dyes from waste streams due to their wide variations in porosity, surface chemistry, higher thermal stability and regenerability on site [21-23].

The objective of this work was to explore the possible use of alumina reinforced polystyrene (ARP) composite as an adsorbent for the removal of amaranth dye. For optimization, effect of various parameters such as contact time, pH, temperature and dye concentration were investigated. The experimental data was fitted to the Langmuir, Freundlich, Temkin and Dubinin–Raduskevich adsorption isotherms. In order to understand the rate and mechanism of adsorption process by
ARP, the adsorption kinetics was also determined. Thermodynamic analysis was used to elucidate the adsorption and desorption mechanism of amaranth dye onto ARP composite.

### 6.2. Materials and Methods

#### 6.2.1. Materials

Commercial polystyrene beads and alumina were purchased from BDH Ltd., India. Acetone and cetyl-tri-methyl-ammonium bromide (CTAB) was purchased from Emerck Ltd. Amaranth dye having the molecular formula – C\textsubscript{20}H\textsubscript{11}O\textsubscript{10}S\textsubscript{3}N\textsubscript{2}Na\textsubscript{3}, C.I.-16185 was purchased from CDH Ltd, India. The structure of amaranth is shown in Fig. 6.1. The solution was prepared by dissolving the appropriate amount of dye in double distilled water.

![Structure of amaranth dye](image)

**Fig. 6.1. Structure of amaranth dye.**

#### 6.2.2. Preparation of Polystyrene - Alumina Composite

A mixture of 5.0 g alumina powder and 5.0 g polystyrene was blended in 50 ml acetone and kept for 5 days. Then, 0.5 g of CTAB was added as a functionalizing agent and placed in ultrasonic bath for 1 h at 40 °C. The above mixture was stirred until the alumina got completely blended into the polystyrene. The acetone was then evaporated and polystyrene–alumina composite was dried at 60 °C. The composite was crushed and sieved to get particle size of 50–100 mesh BSS. The powdered material was washed with double distilled water, subsequently dried at 60 °C and used as such throughout the adsorption studies.

#### 6.2.3. Characterization

The surface morphology of ARP was examined by the scanning electron microscopy using Leo 435 VP model. The FTIR spectra of ARP before and after amaranth adsorption was recorded in the frequency range of 400 – 4000 cm\(^{-1}\) using FTIR spectrophotometer (Inter- spec 2020, Spectro lab, UK) in KBr pellets. Thermal
analysis was performed by (DTG-60H, Shimadzu) in the presence of nitrogen at the flow rate of 35 ml/min and at the heating rate maintained at 20 ºC/ min.

6.2.4. Equilibrium Adsorption Studies

Batch adsorption studies were carried out with 0.05 g of ARP and 20 ml of amaranth dye at desired concentration, pH and temperature. Adsorption kinetics was determined by analyzing the adsorptive uptake of amaranth from its aqueous solution of 25 mg/l concentration at different time. The equilibrium data for developing the isotherms were obtained at different temperatures (30, 40 and 50 ºC) by mixing 0.05 g of ARP with amaranth concentrations of 15, 20, 25, 30, 35 and 40 mg/l for 180 min. After equilibrium, the aqueous phase concentration of dye in the solution was determined by the double beam UV-visible spectrophotometer (Elico SL-164) at max 520 nm. The equilibrium adsorption capacity of ARP was calculated from the following relationship

\[ q_e = \frac{(C_0 - C_e)V}{w} \]  

where \( q_e \) is the equilibrium adsorption capacity in (mg/g), \( C_0 \) and \( C_e \) is the initial dye concentration and at equilibrium in (mg/l), respectively. \( V \) is the volume of solution in (l) and \( w \) is the weight of adsorbent in (g).

6.2.5. Desorption Studies

Desorption studies helps to elucidate the nature of adsorption and recycling of the spent adsorbent. Desorption studies as a function of temperature and different eluent like 0.1M HCl, 0.1M CH₃COOH, 0.1M NaOH and 99% CH₃OH were conducted in batch experiments. Desorption experiments were performed by mixing 0.05 g of dye exhausted ARP with 20 ml of eluent.

6.3. Results and Discussion

6.3.1. Characterization

6.3.1.1. SEM Analysis

Scanning electron microscopy (SEM) is a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of ARP composite is shown in Fig. 6.2. It is clear that, ARP surface appears to be irregular which is probably a good platform for the adsorption of dye molecules.
6.3.1.2. Thermogravimetric Analysis

Thermal analysis of the ARP is shown in Fig. 6.3. The figure shows the first weight loss (5.7%) between 27-150 °C indicating evaporation of water which was physically adsorbed. The second weight loss (4.9%) was observed from 150-399 °C, indicating the decomposition of the intercalated CTAB and evaporation of retained water which was strongly adsorbed by the alumina in the polystyrene layers (most probably in the form of H-bonded water). Lefevre et al. [24] and Alwitt et al., [25] also observed the dehydration peak for alumina between 200- 400 °C. It was further supported by DTA and DSC curves which confirm endothermic peaks due to dehydration in the same temperature range. The major weight loss about 33.3% was observed between 400-699 °C, presumably due to the decomposition of polystyrene. Qing et al., [26] reported the TGA of polystyrene in a single step, beginning at approximately 350 °C and complete about at 500 °C. The increase in the decomposition temperatures may be the result of strong interaction between polystyrene and alumina.
6.3.1.3. Determination of Zero Point Charge

The surface charge of ARP can be determined by the point of zero charge (pHz) study. For the determination of pHz, 0.1 M KCl was prepared, and its initial pH was adjusted between 2.0 and 12.0 using HCl and NaOH. Then, 20 ml of 0.1 M KCl was taken in 100 ml flasks and 0.05 g of ARP was added to each solution. These flasks were kept for 24 h and the final pH of the solutions was measured with a pH meter. Graphs were plotted between initial pH and final pH [18]. From the Fig. 6.4 it is clear that at 6.8, $\Delta$pH = 0, therefore the pHz of ARP is 6.8.
6.3.2. Effect of pH

The pH of the dye solution is an important controlling parameter in the adsorption process. Fig. 6.5 shows the effect of solution pH on amaranth adsorption onto ARP at various initial solution pH for an initial dye concentration of 25 mg/l and ARP dose of 2.5 g/l at 30 ºC. As the pH increased from 2.0 to 9.5, the adsorption capacity decreases and the maximum adsorption was observed at pH 2.0. Similar result was also observed by Gong et al., [27] for the removal of amaranth onto peanut hull. This effect of pH on amaranth adsorption could be explained on the basis of the different activity of functional groups of adsorbent and dye in solution. At pH 2.0, the H⁺ ion concentration in the system increases and the surface of ARP acquires positive charge by absorbing the H⁺ ions. As the ARP is positively charged at low pH, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and the anionic amaranth dye molecules, leading to maximum dye adsorption. As the pH of the system increases, the number of negatively charged sites increases while the number of positively charged sites decreases. Negatively charged sites on the adsorbent do not favor the adsorption of dye anions due to electrostatic repulsion.

In ARP composite, alumina plays an important role in the removal of the amaranth under the influence of the pH. Hence different types of interactions between alumina surface and amaranth molecules may be assumed.
Under acidic condition, alumina undergoes protonation that interact with the negatively charged sulfonic groups of amaranth by the electrostatic forces:

\[
\text{AlOH} + \text{H}^+ \rightarrow \text{AlOH}_2^+ \quad (2)
\]

\[
\text{AlOH}_2^+ + \text{O}_3\text{S}–\text{R} \rightarrow \text{AlOH}_2^+\text{O}_3\text{S}–\text{R} \quad (3)
\]

where R represents the rest of dye molecule.

In basic medium (at pH 9) the surface of alumina becomes negatively charged due to the formation of AlO\(^-\) groups on its surface which repel negatively charged sulfonic groups whereby reducing the adsorption of amaranth.

\[
\text{AlOH} + \text{OH}^- \rightarrow \text{AlO}^- \quad (4)
\]

\[
\text{AlO}^- + \text{O}_3\text{S}–\text{R} \rightarrow \text{AlO}^-\text{O}_3\text{S}–\text{R} \quad (5)
\]

![Fig. 6.5. Effect of pH on amaranth adsorption onto ARP.](image)

### 6.3.3. Adsorption Kinetics

The effect of contact time on the extent of amaranth adsorption is illustrated in Fig. 6.6. The adsorption increases with time and reaches equilibrium within 120 min. Initially the adsorption was fast due to the surface and gradually get slower as dye ions enter into the pores after the saturation of the active surface site.
Adsorption of Amaranth Dye

In order to evaluate the mechanism and potential rate-controlling steps involved in the process of adsorption, pseudo-first order [28], pseudo-second order [29] and Elovich kinetics models [30] were used. The pseudo-first order kinetic model equation is:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where \(q_t\) is the amount of dye adsorbed at time \(t\) in (mg/g), \(k_1\) is the rate constant of the equation in (l/min) and \(q_e\) is the amount of adsorption equilibrium in (mg/g). The adsorption rate constant \((k_1)\) can be determined experimentally by plotting \(\ln (q_e - q_t)\) against \(t\) (Fig. 6.7).

The pseudo-second order kinetic model is expressed as:

\[
t/q_t = 1/k_2 q_e^2 + t/q_e
\]

where \(k_2\) is the equilibrium rate constant of pseudo-second order adsorption in (g/mg min). The values of \(k_2\) and \(q_e\) can be determined from the slope and intercept of the plot (Fig. 6.8) \(t/q_t\) vs. \(t\), respectively.

The Elovich model is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as:

\[
q_t = (1/\beta) \ln (\alpha \beta) + (1/\beta) \ln t
\]

where, \(\alpha\) is the initial adsorption rate in (mg/g min) and \(\beta\) is related to the extent of
Adsorption of Amaranth Dye

The values of R² and several kinetic parameters obtained from applied kinetic models have been tabulated as Table 6.1. The experimental data fitted well to the pseudo-second order kinetic model with a high R² value (0.987) than pseudo-first order (0.9612) and Elovich model (0.9538). Moreover, the value of calculated qₑ is closer to the experimental qₑ value for pseudo-second order kinetics. Similar results for adsorption kinetics have also been reported elsewhere [20, 27, 31].

**Table 6.1. Kinetic parameters for the amaranth adsorption onto ARP.**

<table>
<thead>
<tr>
<th>Pseudo-first order kinetic</th>
<th>Pseudo-second order kinetic</th>
<th>Elovich model</th>
</tr>
</thead>
<tbody>
<tr>
<td>qₑ = 5.442 (mg/g)</td>
<td>qₑ = 7.836 (mg/g)</td>
<td>α = 0.459 (mg/g min)</td>
</tr>
<tr>
<td>k₁ = 0.021 (1/min)</td>
<td>k₂ = 5.063 × 10⁻³ (g/mg min)</td>
<td>β = 0.67 (g/mg)</td>
</tr>
<tr>
<td>R² = 0.9612</td>
<td>R² = 0.9873</td>
<td>R² = 0.9538</td>
</tr>
</tbody>
</table>

**Fig. 6.7. Pseudo-first order kinetic model for amaranth adsorption.**
6.3.4. Diffusion Mechanism

The transport of dye from the solution phase to the surface of adsorbent occurs in several steps:

(i) Diffusion of dye molecules through the solution to the adsorbent surface

(ii) Adsorption of dye molecules on the surface of the material through the molecular
(iii) Diffusion of dye molecules from the surface into the interior of the adsorbent material

(iv) Adsorption of dye molecules at an active site on the material surface (chemical reaction via ion-exchange, complexation or chelation [32].

To determine rate limiting step (either film diffusion or intraparticle diffusion) as well as the corresponding rate constants, the kinetic data was further processed. The intraparticle diffusion model equation proposed by Weber and Morris and film diffusion model equation proposed by McKay can be written as [33]:

Intraparticle diffusion model: 
\[ q_t = K_d t^{1/2} + C \]  
\[ F = \frac{q_t}{q_\infty} \]  

where \( K_f \) is the diffusion rate parameter in film diffusion model, \( K_d \) is the diffusion rate parameter in intraparticle diffusion model, \( F \) is the fractional attainment of the equilibrium and \( q_t \) and \( q_\infty \) are amounts of dye adsorbed after time \( t \) and infinite time, respectively.

If intraparticle diffusion is involved in the adsorption process, the plot of \( q_t \) vs \( t^{1/2} \) would result in a linear relationship and the intraparticle diffusion would be the controlling step if this line passed through the origin. If the plot does not pass through the origin, this is indicative of some degree of boundary layer control which further suggested that the intraparticle diffusion is not the only rate controlling step, but other processes are also controlling the rate of adsorption [32]. From Fig. 6.10 and 6.11, it can be observed that none of the straight lines passes through the origin, which indicates that both intraparticle diffusion and film diffusion are the rate limiting steps for the adsorption of amaranth onto ARP [34, 35]. The above two conclusions suggest that all three mechanisms: intrinsic surface reaction, film mass transfer and intraparticle diffusion are rate-limiting step [35].
6.3.5. Modeling of Adsorption Equilibrium

Fig. 6.10. Weber and Morris plot of \( q_t \) vs. \( t^{1/2} \) for amaranth adsorption,
\[
K_d = 0.5645 \text{ mg/g min}^{1/2}.
\]

Fig. 6.11. McKay's plot of \( \ln(1-F) \) vs. \( t \) for amaranth adsorption.

Fig. 6.12 represents the amount of the amaranth adsorbed onto ARP at 30, 40 and 50 °C. It was observed that there is an increase in the amount of amaranth adsorption when the initial dye concentration and temperature increased from 15 to 40 mg/l and 30 to 50 °C, respectively. The larger adsorption capacity of ARP at higher
dye concentration was possible due to the greater driving force by the concentration gradient \( \Delta C = C_o - C_e \) [36]. The increase in the adsorption capacity with the increases in temperature suggests endothermic nature of the adsorption. The increase in adsorption capacity results from the increase in collision frequency between adsorbent and adsorbate, which results in the enhanced adsorption onto the surface of the adsorbent. Furthermore, the enhancement of adsorption capacity may be due to the formation of new reaction sites or the increased rate of intraparticle diffusion of dye molecules into the pores of the adsorbent at higher temperature [37].

\[
\begin{align*}
\text{Langmuir model:} & \quad C_e/q_e = C_e/q_m + (1/ q_m b) \\
\text{Freundlich model:} & \quad \ln q_e = \ln K_F + (1/n) \ln C_e \\
\text{Temkin model:} & \quad q_e = B \ln A + B \ln C_e \\
\text{D–R Model:} & \quad \ln q_e = \ln q_m - B \frac{1}{C_e} \\
\Sigma & = RT \ln (1 + 1/C_e) \\
E & = \frac{1}{2 B_1}
\end{align*}
\]

where \( C_e \) is the equilibrium dye concentration in the solution (mg/l), \( b \) is the

---

Fig. 6.12. Effect of concentration on amaranth adsorption onto ARP at different temperature

In order to calculate the adsorption capacity of ARP, the experimental equilibrium data were fitted to the Langmuir [38], Freundlich [39], Temkin [40] and Dubinin–Raduskevich [41] isotherm equations. Linear equations of all the applied models are:

- **Langmuir model**: \( C_e/q_e = C_e/q_m + (1/ q_m b) \) (12)
- **Freundlich model**: \( \ln q_e = \ln K_F + (1/n) \ln C_e \) (13)
- **Temkin model**: \( q_e = B \ln A + B \ln C_e \) (14)
- **D–R Model**: \( \ln q_e = \ln q_m - B \frac{1}{C_e} \) (15)
  \( \Sigma = RT \ln (1 + 1/C_e) \) (16)
  \( E = \frac{1}{2 B_1} \) (17)
Langmuir adsorption constant (l/mg) and \( q_m \) is the theoretical maximum monolayer adsorption capacity (mg/g). \( K_F \) (l/mg) and \( n \) are Freundlich isotherm constants indicating the capacity and intensity of the adsorption, respectively. \( A \) is equilibrium binding constant (l/mg) and \( B \) is related to the heat of adsorption. \( B_1 \) is the D–R model constant (\( \text{mol}^2 \text{kJ}^{-2} \)) related to the mean free energy of adsorption per mole of the adsorbate and \( \Sigma \), is the polanyi potential. \( E \) is mean free energy of adsorption (kJ/mol). The values of isotherm parameters are presented in Table 6.2. In all cases, D-R isotherm has highest correlation coefficients, which is a considerably better fit compared with Langmuir, Freundlich and Temkin adsorption isotherms. Furthermore, the values of calculated \( q_m \) is close to the experimental \( q_e \) values at the equilibrium at all the temperatures for D – R isotherm. The magnitude of \( E \) determines the type of adsorption process. The values of \( E \) were found to be 0.849-1.979 kJ/mol. Helfferich [42] and Dang et al., [43] have reported that for adsorption with \( E \) between 8-16 kJ/mol, the process follows chemisorption while physical adsorption corresponds to \( E \) less than 8 kJ/mol. Therefore, the adsorption of amaranth onto ARP can be considered to be influenced by physical forces.

Table 6.2. The values of isotherm parameters for the removal of amaranth dye.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30 °C</td>
</tr>
<tr>
<td><strong>Langmuir model</strong></td>
<td>( q_m ) (mg/g)</td>
<td>14.619</td>
</tr>
<tr>
<td></td>
<td>( b ) (l/ mg)</td>
<td>0.281</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.8695</td>
</tr>
<tr>
<td><strong>Freundlich model</strong></td>
<td>( K_F ) (mg/g)</td>
<td>0.775</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9171</td>
</tr>
<tr>
<td><strong>Temkin model</strong></td>
<td>( B )</td>
<td>3.354</td>
</tr>
<tr>
<td></td>
<td>( A ) (l/ mg)</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9434</td>
</tr>
<tr>
<td><strong>D – R Model</strong></td>
<td>( q_m ) (mg/g)</td>
<td>8.281</td>
</tr>
<tr>
<td></td>
<td>( B_1 ) (( \text{mol}^2 \text{kJ}^{-2} ))</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>( E ) (kJ/mol)</td>
<td>1.979</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.985</td>
</tr>
</tbody>
</table>
6.3.7. Thermodynamic Studies

The standard free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) thermodynamic parameters have been estimated to evaluate the feasibility of the adsorption process. The thermodynamic parameters were determined by using the following equations:

$$\Delta G = -RT \ln K_c$$  \hspace{1cm} (18)

$$\ln K_c = (\Delta S^0/R) - (\Delta H^0/RT)$$  \hspace{1cm} (19)

where $K_c$ is the distribution coefficient for the adsorption. R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). The values of $\Delta H^0$ and $\Delta S^0$ are calculated from the slope and intercept of the plots of $\ln K_c$ vs. 1/T. The negative values of $\Delta G^0$ (–1.898, –2.457 and –3.721 kJ/mol) increased with temperature at 30, 40 and 50 °C, respectively, indicating the feasibility and spontaneity of the adsorption process. The values of the standard enthalpy and the entropy changes were determined and found to be 24.89 kJ/mol and 0.088 kJ/mol K ($R^2 = 0.9379$), respectively. The positive value of $\Delta H^0$ further confirms the endothermic nature of the adsorption process while the positive $\Delta S^0$ values suggest increase in randomness at the solid–liquid interface during adsorption [44].

The attraction between adsorbate and adsorbent arises from van der Waals forces, hydrophobicity, hydrogen bonds, ligand exchange, dipole–dipole interactions and chemical bonds. The energy released by different forces during adsorption is unequal [22, 45] and the energy associated with the physical and chemical forces are van der Waals forces (4–10 kJ/mol), hydrophobic bond forces (5 kJ/mol), hydrogen bond forces (2–40 kJ/mol), coordination exchange (40 kJ/mol), dipole bond forces (2–29 kJ/mol) and chemical bond forces (>60 kJ/mol). In this study, the enthalpy change associated with amaranth adsorption onto ARP is 24.89 kJ/mol, suggesting that all the above mentioned forces except coordination exchange and chemical bond forces were involved for adsorption of amaranth.

6.3.8. FTIR Analysis

The FTIR spectra of the ARP before and after adsorption are given in Fig. 6.13. The absorption band at 3431 cm$^{-1}$ corresponds to the O–H stretching frequency of water. The bands in the 3059–2852 cm$^{-1}$ region are attributed to the stretching of C–H. The absorption peaks for polystyrene that appear in the regions of 1631 and
697 cm\(^{-1}\) are due to the aromatic C-H bonds and the out of plane benzene ring C-C bond, respectively [46]. The peak at 1602 cm\(^{-1}\) is assigned to the O–H bending mode of water or vibration of C–C bonds in the benzene ring. The peaks at 1492 and 1449 cm\(^{-1}\) are attributed to the CH\(_2\) scissoring mode of vibration and indicates close-packing of the methylene chains of CTAB or due to the vibration of C–C bonds in the benzene ring of polystyrene [46,47]. The absorption peaks at 1070 and 752 cm\(^{-1}\) are the characteristic absorption of C–N of CTAB and Al–OH bond, respectively. When compared with the FTIR spectra of ARP after dye adsorption (Fig. 6.13b), the intensity of some bands changed and the new absorption bands at 1367, 1182 and 1153 cm\(^{-1}\) were observed, which may be attributed to O–H and asymmetric vibration of S–O groups of amaranth, respectively. It seems that these groups are the main functional groups which participate in the binding of dye onto the adsorbent. Gong et al., [27] have also reported that hydroxyl group plays important role in the adsorption of amaranth onto peanut hull.

**Fig. 6.13.** FTIR spectra of ARP (a) before adsorption and (b) after adsorption.

**3.9. Effect of Temperature on Desorption and Thermodynamics.**

Desorption experiments were performed using 0.1 M HCl, 0.1 M CH\(_3\)COOH, 0.1 M NaOH and 99% CH\(_3\)OH as eluent. It was observed that 0.1 M HCl and 0.1 M CH\(_3\)COOH did not show any desorption. The effect of temperature on desorption was studied at 30, 40 and 50 °C and the results are depicted in Fig. 6.14. The amount of
amaranth desorption by 20 ml of 0.1 M NaOH and CH₃OH solutions increases with the increase in temperature and it was found that higher temperature facilitated the desorption of amaranth in both eluent. This may be attributed to the increase in the solubility of dye into eluent and increasing temperature may produce a swelling effect within the internal structure of adsorbent, which diffuse the dye molecule from pores to solution. Thermodynamics parameters i.e. free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were calculated using Van’t Hoff and Gibb’s –Helmholtz equations (eq. 18 and 19) for the desorption of amaranth. Thermodynamic parameters of desorption evaluated at different temperatures are presented in Table 6.3. The values of the free energy change ($\Delta G^0$) were negative, confirming that the desorption processes was spontaneous and thermodynamically favorable. The higher negative values of ($\Delta G^0$) imply the greater driving force leading to higher desorption. Free energy change for desorption obtained with 0.1 M NaOH is greater than that obtained with CH₃OH, indicating that 0.1 M NaOH is a more favorable eluent for desorption than CH₃OH. The positive $\Delta H^0$ value indicates that desorption of amaranth is endothermic in nature and the positive value of entropy ($\Delta S^0$) indicates an increase in randomness at the solid-liquid interface.

![Graph showing effect of temperature on amaranth desorption from saturated ARP.](image)

**Fig. 14. Effect of temperature on amaranth desorption from saturated ARP.**
Table 6.3. Thermodynamic parameters for the desorption of amaranth from ARP.

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Temperature (°C)</th>
<th>$\Delta G^\circ$ (kJ/ mol)</th>
<th>$\Delta H^\circ$ (kJ/ mol)</th>
<th>$\Delta S^\circ$ (kJ/ mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH (99%)</td>
<td>22</td>
<td>$-0.201$</td>
<td>$26.604$</td>
<td>$0.091$</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>$-1.725$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>$-2.275$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>22</td>
<td>$-3.491$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>$-5.183$</td>
<td>$51.831$</td>
<td>$0.186$</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>$-7.905$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.4. Conclusion

The aim of this work was to explore the possible use of ARP composite as an adsorbent for the removal of amaranth dye from aqueous solution. From batch kinetics studies it was found that the adsorption of amaranth onto ARP followed the pseudo-second order kinetic model while film diffusion and intraparticle diffusion being the rate limiting step. Thermodynamic calculations indicated that the adsorption process is endothermic in nature and therefore, the amaranth removal increased with increases in temperature. The enthalpy change of amaranth adsorption onto ARP is 24.89 kJ/ mol, suggesting that the physical forces were involved for adsorption of amaranth. FTIR analysis indicated that OH$^-$ and SO$_3^{-}$ groups of amaranth were mainly involved in the adsorption of amaranth onto ARP. Desorption study revealed that CH$_3$OH and 0.1 M NaOH can elute upto 70 and 96% of amaranth respectively, from the amaranth saturated ARP at 45 °C.