Removal of Tartrazine Dye form Aqueous Solutions by Adsorption on the Surface of Polyaniline/Iron Oxide Composite

Salem Ali Jebreil

Abstract—In this work, a polyaniline/Iron oxide (PANI/Fe$_3$O$_4$) composite was chemically prepared by oxidative polymerization of aniline in acid medium, in presence of ammonium persulphate as an oxidant and amount of Fe$_3$O$_4$. The composite was characterized by a scanning electron microscopy (SEM). The prepared composite has been used as adsorbent to remove Tartrazine dye form aqueous solutions. The effects of initial dye concentration and temperature on the adsorption capacity of PANI/Fe$_3$O$_4$ for Tartrazine dye have been studied in this paper. The Langmuir and Freundlich adsorption models have been used for the mathematical description of adsorption equilibrium data. The best fit is obtained using the Freundlich isotherm with an $R^2$ value of 0.998. The change of Gibbs energy, enthalpy, and entropy of adsorption has been also evaluated for the adsorption of Tartrazine onto PANI/Fe$_3$O$_4$. It has been proved according the results that the adsorption process is endothermic in nature.

Keywords—Adsorption, Composite, dye, Polyaniline, Tartrazine.

I. INTRODUCTION

Electrically conducting polymers are important in modern technology as they have potential applications in optical and micro-electronic devices, chemical sensors [1], catalysis, anti corrosion, and energy storage systems [2], [3]. Polyaniline is one of the most interesting conducting polymers due to its environmental stability [4]. Practically, Polyaniline can be prepared via chemical or electro-chemical oxidation of aniline in acidic medium [5], [6].

Conducting polymer/inorganic particle composites with different combinations of the components have attracted more attention since they have interesting physical properties. A variety of oxides such as: Al$_2$O$_3$, TiO$_2$, MnO$_2$, and Fe$_3$O$_4$ have been incorporated into Polyaniline in order to improve its properties [7]-[10].

Color pollution in aquatic environments is an escalating problem. The recalcitrant nature of modern synthetic dyes has led to the imposition of strict environmental regulations. The need for a cost effective process to remove the color from wastewater produced by the textile industry, has been recognized.

Dyes are one of the organic compounds which can color other substances and make them brighter. Synthetic dyes generally have a complex aromatic molecular structure which it probably comes from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. Due to the complex aromatic molecular structure of dyes, these dyes will be more stable and harder to biodegrade [11], [12]. The main technologies used for the treatment of dye-containing effluents are chemical precipitation, adsorption, ion exchange, biodegradation, membrane filtration, coagulation, flocculation, etc. Adsorption is widely used and it is the most versatile as other methods have high capital cost and low efficiency [13], [14].

In this paper, adsorption of Tartrazine dye from aqueous solution on the surface of Polyaniline/Iron oxide (PANI/Fe$_3$O$_4$) has been investigated. Furthermore, thermodynamic parameters of adsorption have been calculated using Freundlich and Langmuir equations.

The effect of temperature in the range of 20-40°C has been studied. It has been found that the amount of adsorption increases when temperature increases. Freundlich and Langmuir equations have been applied for the obtained results.

II. MATERIALS AND METHODS

A. Materials

The materials have been used in this research are as follows: Aniline (PARK) which was used after double distillation, Ammonium persulfate, pure Fe$_3$O$_4$ (99%), Acetone and Hydrochloric acid (obtained from BDH), and Tartrazine dye (Aldrich, USA) which were used without further purification.

<table>
<thead>
<tr>
<th>Parameter Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C$<em>{19}$H$</em>{33}$N$_7$Na$_3$O$_6$S$_2$</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>554.36</td>
</tr>
<tr>
<td>C.I. No</td>
<td>19160</td>
</tr>
<tr>
<td>Physical form</td>
<td>Orange powder</td>
</tr>
<tr>
<td>Soluble in solvents</td>
<td>Water</td>
</tr>
<tr>
<td>$\lambda_{max}$ (nm)</td>
<td>426</td>
</tr>
<tr>
<td>C.I. Name</td>
<td>Anionic Dye</td>
</tr>
</tbody>
</table>

B. Methods

1. Dye Solution Preparation

The characteristics of the Tartrazine are given in Table I while Fig. 1 illustrates the Chemical structure of Tartrazine. An accurately weighed quantity of the dye (0.534g) was dissolved in double distilled water to prepare stock solution (1x10^-5 M). This solution has been used in the experiments to...
get the desired concentration by successive dilutions, which ranges from $5 \times 10^{-5}$ to $1.25 \times 10^{-4}$ M.

\[ \text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1) \]

where $C_0$ is the initial concentration of the dye and $C_e$ is the equilibrium concentration of the dye (mol/L).

The equilibrium adsorption capacity of PANI/Fe$_2$O$_3$ for Tartrazine dye has been calculated from the following relationship:

\[ q_e = \frac{(C_o - C_e)V}{W} \quad (2) \]

where $q_e$ is the equilibrium adsorption capacity, $C_e$ is the dye concentration (mol · L$^{-1}$) at equilibrium, $V$ is the volume (L) of solution, and $w$ is the weight (g) of adsorbent.

The amount of Tartrazine dye adsorbed $q_t$ at time $t$ onto the surface of the PANI/Fe$_2$O$_3$ has been estimated by the mass balance equation as follows:

\[ q_t = \frac{(C_0 - C_t)V}{W} \quad (3) \]

Equilibrium Experiments

The effect of the initial dye concentration has been determined by placing 0.03 g of the PANI/Fe$_2$O$_3$ composite in 20 ml of dye solution of different initial concentrations ($5 \times 10^{-5}$ M, $7.5 \times 10^{-5}$ M, $1 \times 10^{-4}$ M and $1.25 \times 10^{-4}$ M) for 60 minutes at $30 \pm 1^\circ$C. The concentration of Tartrazine dye left in the supernatant solution was determined by spectrophotometer at a wavelength of maximum absorbance (426 nm).

III. RESULTS AND DISCUSSION

A. Surface Morphology Analysis

The scanning electron microscopy (SEM, JMS-6700F) image of PANI/Fe$_2$O$_3$ is shown in Fig. 2. It can be seen from the figure that the surface is irregular and porous, which provides a good platform for Tartrazine adsorption.

B. Effect of Initial Dye Concentration

The effect of initial dye concentration on adsorption efficiency onto PANI/Fe$_2$O$_3$ has been explored as shown in Fig. 3. The examined dye concentration on adsorption is in the range of $5 \times 10^{-5}$ to $1.25 \times 10^{-4}$ (mol·L$^{-1}$) Tartrazine at temperature $30 \pm 1^\circ$C in presence 0.03 g PANI/Fe$_2$O$_3$. It can be noticed from the figure that the percentage of Tartrazine
removal has decreased with the increase in initial concentration of Tartrazine. Although the percent of adsorption has decreased with the increase in initial dye concentration, the actual amount of dye adsorbed per unit mass of adsorbent has increased with increase in dye concentration. This is because the initial dye concentration supplies the required driving force in order to overcome the resistance facing the mass transfer ofTartrazine between aqueous phase and the solid phase. The increase in initial dye concentration causes an increase in the interaction between dye molecules and PANI/Fe\textsubscript{2}O\textsubscript{3} surface. As a result, the increase of the initial concentration of Tartrazine improves the adsorption uptake of the dye [16].

It can be noticed from Table II that the value of \( K_f \) increases with the increase of temperature. This means that the adsorption process increases with increase in temperature (i.e. the process is endothermic). Fig. 4 shows the application of Freundlich on adsorption results at different temperature.

\begin{align}
\text{Langmuir Isotherm Modeling}
\end{align}

\begin{align}
\ln q_{eq} &= \ln K_f + \frac{1}{n} \ln C_{eq}
\end{align}

where: \( q_{eq} \) is the amount of dye adsorbed at equilibrium, \( K_f \) is Freundlich constant related to the sorption, \((1/n)\) is an empirical parameter related to sorption intensity, which varies heterogeneity of the material and \( C_{eq} \) is the equilibrium dye Concentration in solution.

It can be noticed that when Freundlich equation has been applied, the obtained results were compatible with the equation, where correlation coefficient (R\textsuperscript{2}) was approximately 0.998 in most of the cases, as it appears in Fig. 4. Table II shows the values of \( K_f \) and \( n \) of Tartrazine dye.

\begin{table}[h]
\centering
\caption{Freundlich Adsorption Constants for Adsorption of Tartrazine PANI/F\textsubscript{2}O\textsubscript{3} at Different Temperature}
\begin{tabular}{|c|c|c|c|c|}
\hline
Temp (°C) & \( R^2 \) & \((1/n)\) & \( n \) & Ln\( K_f \) & \( K_f \) \\
\hline
20 & 0.996 & 0.155 & 6.45 & -1.05 & 0.355 \\
25 & 0.999 & 0.156 & 6.41 & -0.947 & 0.387 \\
30 & 0.981 & 0.171 & 5.84 & -0.677 & 0.508 \\
35 & 0.997 & 0.217 & 4.60 & -0.013 & 0.987 \\
40 & 0.996 & 0.242 & 4.13 & 0.402 & 1.490 \\
\hline
\end{tabular}
\end{table}

\begin{align}
\frac{C_{eq}}{q_{eq}} &= \frac{1}{K_f q_{max}} C_{eq}
\end{align}

where \( C_{eq} \) is the equilibrium concentration of the dye (mol/L), \( q_{eq} \) is the amount of adsorbate dye per each gram of composite at equilibrium, \( q_{max} \) (mmol/g) is the maximum amount of adsorbed dye corresponding to complete monolayer coverage, \( K_f \) (L/mol) is the Langmuir adsorption equilibrium Constant related to the energy of adsorption. The Langmuir constants can be evaluated from the slope and the intercept of the linear equation.
Fig. 5 shows the application of Langmuir equation for the results of Tartrazine dye adsorbing on the surface of PANI/Fe₃O₄ composite at different values of temperature.

\[ \ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \]  

\[ \Delta G = \Delta H - T\Delta S \]

First of all, a graph of \( \ln K_c \) on the Y-axis and \( 1/T \) on the X-axis is plotted as shown in Fig. 5. The relationship is linear with a slope equals \( -\frac{\Delta H}{R} \).

Table IV gives the quantitative thermodynamic data of dye adsorption process of Tartrazine onto PANI/Fe₃O₄, while the positive value of \( \Delta S \) revealed the increase in randomness at the solid-solution interface during the adsorption process.

**G. Weber–Morris Model**

The Intraparticle diffusion model has been tested in order to identify the adsorption mechanism. The Intraparticle diffusion model de-signed by Weber–Morris [20] is given in the following equation:

\[ \ln K = \frac{R^2}{D_{SO}} \]

Where: \( \Delta G \) is change in free energy (KJ/mol), \( R \) is general gas constant, which equals 8.314/J/mol.k, \( T \) is Absolute temperature (K), \( K_l \) is Langmuir constant (L/mol).

Equations (8) and (9) are used to calculate the values of \( \Delta S, \Delta H \):
where: $K_i$ is the Intraparticle diffusion rate constant in (mmol.g^{-1}.min^{-0.5}), $t_0^{0.5}$ is square root of contact time; I is an intercept (mmol. g^{-1}) proportional to the boundary layer thickness.

It should be noticed that the larger value of I, the greater is the boundary layer effect [21], [22].

When Weber–Morris model has been applied on the results of adsorption process obtained in this research, it has been found that graphical shape of this model has linear intersects with Y-axis while it does not passes through the origin, as shown in Fig. 7. This means that the adsorption process is complicated. It also means that both surface adsorption mechanism and adsorption due to diffusion inside Polyamine iron oxide composite are the responsible for the completion of adsorption process.

The value of intercept gives an indication about the thickness of the boundary layer. When intercept is larger the effect of thickness of the diffusion layer will be greater in adsorption process.

It can be concluded that the amount of adsorbed dye on the surface of (PANI/Fe_{3}O_{4}) is the sum of adsorption on the surface and the adsorption inside the composite. It can also be noticed that the value of $R^2$ approaches one which indicates that the application of this model on the results is correct.

Table V shows the values of intercepts (I) and $K_i$ which are calculated by Weber–Morris model on the results of Tartrazine dye adsorption at different initial dye concentration.

**IV. CONCLUSIONS**

A polyaniline/Iron oxide (PANI/Fe_{3}O_{4}) composite has been chemically prepared by oxidative polymerization of aniline in medium acid, in presence of ammonium persulphate as an oxidant and amount of Fe_{3}O_{4}. This composite has been used to remove Tartrazine dye from aqueous Solution. It has been noticed from this study that physical adsorption is the responsible process for removal of Tartrazine dye from aqueous solutions. It has also been concluded that the amount of adsorbed dye on the surface of (PANI/Fe_{3}O_{4}) is the sum of adsorption on the surface and the adsorption inside the composite. Furthermore, according to the obtained results, the process is endothermic process. It has been also noticed the percentage of Tartrazine removal decreases with the increase in initial concentration of Tartrazine.

**ACKNOWLEDGMENT**

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**REFERENCES**

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**TABLE V**

<table>
<thead>
<tr>
<th>[Dye] mol/L</th>
<th>Intercept (I)</th>
<th>$K_i$</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>5 x 10^{-3}</td>
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<td>1.77 x 10^{-4}</td>
<td>0.942</td>
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<tr>
<td>7.5 x 10^{-3}</td>
<td>2.99 x 10^{-3}</td>
<td>3.40 x 10^{-4}</td>
<td>0.937</td>
</tr>
<tr>
<td>1 x 10^{-3}</td>
<td>3.28 x 10^{-3}</td>
<td>5.25 x 10^{-4}</td>
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</tr>
<tr>
<td>1.25 x 10^{-3}</td>
<td>2.22 x 10^{-3}</td>
<td>9.61 x 10^{-4}</td>
<td>0.969</td>
</tr>
</tbody>
</table>

**Fig. 7** Intreapartical diffusion plot for adsorption of Tartrazine onto PANI/Fe_{3}O_{4} at various dye concentrations

It can be noticed from Table V that the values of $K_i$ increase by the increase of initial dye concentration. This can be interpreted according to the effect of potential force due to the gradual change in concentration.


