Elimination Study of Methylene Blue Dye Using PANI and PANI/SiO2 Composite.

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Elimination study of methylene blue dye using PANI and PANI/SiO\textsubscript{2} composite.

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Abstract

Conducting Polymeric composites have attracted great attention over the last years because of their potential uses in chemical, electronic and optical devices, and as catalysts as well as in adsorption processes. Chemical synthesis of polyaniline (PANI) and polyaniline-SiO\textsubscript{2} composite and their adsorptive performance were reported in the present work. These materials were prepared and evaluated for their methylene blue (MB) dye adsorption characteristics from aqueous solution. Adsorption equilibrium kinetic and thermodynamic experiments of MB onto PANI and PANI/SiO\textsubscript{2} were studied. The effects of initial dye concentration, contact time and temperature on the adsorption capacity of PANI/SiO\textsubscript{2} for MB have been investigated. The pseudo-first order and pseudo-second order kinetic models were used to describe the kinetic data. It was found that adsorption kinetics followed the pseudo-second order at all of the studied temperatures. The Langmuir, Freundlich and Dubinin Raduschkevich adsorption models were used for the mathematical description and the fit obtained using the Dubinin Raduschkevich isotherm has a medium $R^2$ value.

Keywords: Polyaniline, polyaniline composite, adsorption, methylene blue dye, Langmuir isotherm.

1. Introduction:

With the rising awareness of the occurrences of industrial activities, numerous deteriorations on several ecosystems have been intensified and have started to seriously threaten the human health and environment. Among the many instances of pollution of aqueous media, dye contamination of waters occurs when a wide spectrum of chemicals and dyes are discharged directly or indirectly into water bodies without adequate treatment to remove and degrade these harmful compounds. More than 100,000 commercially available dyes are known and approximately 1 million tons of these dyes are
produced annually worldwide. The major sources of dye contamination are considered to be from textiles industry [1]. The effective removal of dyes from aqueous wastes is an important issue for many industrialised countries. The traditional treatment methods used to remove dyes from wastewaters have certain disadvantages such as incomplete dye removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require further disposal [2]. However, these techniques are non-destructive, since they only transfer the non-biodegradable matter (dyestuffs) into sludge, thus giving rise to a new type of pollution, which needs further treatment. In principle, it is very difficult to treat dye laden wastewaters due to their high solubility and complex molecular structures. However, the adsorption technique is being considered a most appropriate technique. This is because adsorption is relatively simpler, much selective, cost-effective, and easy to operate and a proven efficient process for the removal of dyes from contaminated aqueous media [3]. In recent years, conjugated polymers, particularly those based on polyaniline (PANI), polythiophene (PT) and their derivatives, have gained popularity as chemical adsorbents because of multiple properties such as the low cost synthesis and their numerous applications in rechargeable batteries, display devices and sensors, porous structure, tunable morphology, good electrorheological property, unique redox chemistry, non-toxicity, insolubility in water and reversible ions sorption and desorption capability, environmental stability, their simple doping and dedoping by acid/base treatment have made them very interesting agents in conducting polymers family [4-10]. Recently, a great work has been made to combine conjugated polyaniline with conventional organic and inorganic adsorbents to form composites or hybrid adsorbents such as PANI-graphene Oxide [11], doped polyaniline-potash alum [12], polyaniline-polystyrene (PANI-PS) [13], PANI-cellulose [14] PANI-cellulose fiber [15], polyaniline - polyethylene glycol (PANI-PEG) [16], polyaniline-magnetite [17], PANI-chitosan [18], PANI-sawdust [19], polyaniline-multiwalled carbon nanotubes (PANI-MWCNT) [20], PANI-chitin [21], PANI-nickel ferrite [22]. Though, these materials have been studied like adsorbents for removing dyes, heavy metals and ions from aqueous solutions [23-32] and demonstrate an important attention because of their excellent adsorption performance [33-36]. The aim of this work is the study of the mechanistic nature of blue methylene removal in aqueous solutions at acidic and basic mediums by adsorption using synthesized polyaniline (PANI) and its
silicone composite (PANI-SiO$_2$). For this purpose, a combination of adsorption isotherms, kinetic models are used.

2. Experimental section:

2.1 Synthesis of polyaniline emeraldine salt (PANI-ES)

PANI-ES can be synthesized from monomeric aniline (99.5%, Biochem) by oxidative chemical polymerization [37, 38]. In summary, PANI was prepared as follows: the first solution was prepared with 0.5 M of aniline dissolved in 100 ml of 1M HCl (32%, VWR) and the second solution with 0.25 M of (NH$_4$)$_2$S$_2$O$_8$ (98%, VWR) in 100 ml of distilled water. The latter was added slightly to the first solution with continuous stirring. The mixture was placed under stirring for one hour at 0-5 °C. The greenish black precipitate resulting from this solution was passed to filtration and washing repeatedly with water first, diluted HCl solution and methanol until the wash liquid was colorless to remove oligomers and other non-polymeric impurities. Then, the collected polymer was dried for 48 hours in a 40 °C oven, grinded and stored for processing [39-47].

2.2 Synthesis of PANI/Silica (SiO$_2$) composite:

Determined amount of silica suspension (including 0.23 g of silica / 10 ml), aniline (9.313 g, 0.10 mol) and 10 ml of conc. HCl in 200 ml of distilled water was added by mixing in the ice water bath. The mixtures were stirred for a further 30 minutes. Then, a volume of 100 ml of aqueous APS solution (containing 22,820 g, 0.10 mol of APS) was dropped into the emulsions in 60 minutes. The mixture was placed under stirring for another 4 hours in a cooled water bath. The PANI/silica composite was filtered and washed with water and ethanol three times. Finally it was dried in the oven at 40 ° C for 48 hours [48-52].

2.3 Sorbate dye (Methylene Blue)

To prepare the MB solution 1g of MB was dissolved in 1L of distilled water. It has a molecular formula C$_{16}$H$_{18}$N$_3$ClS with molecular weight 319.85. It is a non-toxic water soluble dye, blue in color ($\lambda_{\text{max}}$ 661 nm). [50, 53] Initial and final concentrations of MB solutions were determined by measuring absorbance at 661 nm using UV visible absorption spectroscopy.

2.4 Adsorption experiments
The adsorption study was performed using an aqueous MB dye solution for the determination of adsorption capacity of the synthetic PANI and PANI/SiO\textsubscript{2} composite. Sample concentrations were determined in the UV-visible apparatus at $\lambda = 661$ nm. The effect of different parameters was carried out from this study such as the adsorption time (0-120 min), the initial concentration in MB (4 - 21 mg / L) and the mass of the adsorbents (0.05 - 1.0 g).

The $q_e$ (equilibrium adsorption amount) was calculated as follows:

$$ q_e = \frac{(C_i - C_e) \cdot V}{m} \ldots \ldots (1) $$

where $C_i$ and $C_e$ are the initial concentration (before adsorption) and concentration at equilibrium (after adsorption) in mg.L$^{-1}$ of MB, respectively; $V$ and $m$ are the volume (L) of the MB solution and the weight (g) of the used material (adsorbent) [54-58].

3. Result and discussion

3.1 Study of adsorption of the dye (MB):

3.1.1 The influence of the contact time

The contact time effect on the quantity of adsorbed methylene blue dye is shown in Figure 1 (a, b).

First, it was seen that the MB concentration after adsorption decreases continuously when the contact time increases with the two adsorbents PANI and PANI/SiO\textsubscript{2} composite.

Also, the dye removal rate is faster in the first 25 minutes, which is due to the large number of free sites for adsorption of MB; therefore, it reaches equilibrium in the 60\textsuperscript{th} minutes and subsequently remains constant. The quantity of MB adsorbed $q_t$ increases from 3.53 mg.g$^{-1}$ in the acidic medium to 5.2 mg.g$^{-1}$ in the alkaline medium when the PANI homopolymer is used. With the PANI/SiO\textsubscript{2} composite, the amount of adsorbed dye $q_t$ increases from 2.23 mg.g$^{-1}$ in acidic medium to 6.97 mg.g$^{-1}$ in alkaline medium.

By comparing the effect of the medium (acidic or alkaline), the PANI homopolymer and the PANI/SiO\textsubscript{2} composite exhibit high adsorption efficiencies in the alkaline medium compared to those in the acidic medium, this can be explained for PANI/SiO\textsubscript{2} by the fact that the particles are more and more negatively charged as the pH becomes more and more basic. This is due to the deprotonation of
surface silanols (Si-OH) by OH⁻ hydroxyls in solution to form silanolates (SiO⁻). For the PANI, the ES form transforms into the EB form at higher pH. The negative charged surface revealed and the negative charge density increased with the increasing pH value. Therefore, the adsorption capacity increased with the increasing pH value.

3.1.2 Effect of adsorbent dosing:

With increasing the adsorbent mass, the number of adsorption sites increases, which consequently increases the adsorption of more dye molecules. By checking the Figure 1(c), it was seen a decrease in the values of \( q_e \) (mg.g\(^{-1}\)) with increasing the mass of PANI and PANI/SiO\(_2\) composite from 0.05 to 1 g. The marginal improvement in the adsorption of the dye can be explained by the reason that a fixed volume of dye solution with a known \( C_o \) of dye has a defined number of total dye molecules and in this condition the dose of adsorbent becomes very important. Therefore, many adsorbent adsorption sites remain empty, resulting in a decrease in \( q_e \) [59]. Consequently, selecting the appropriate dose becomes a very important factor for an effective, efficient treatment process. In this case, the 0.133 g adsorbent mass was selected for all adsorption studies.

Of the two adsorbents used in the study, the PANI/SiO\(_2\) composite exhibits greater elimination at all levels of the adsorbent dosing than pure PANI.

3.1.3 Effect of the dye initial concentration:

It was seen from the figure 1(d) that the dye adsorption increases almost linearly with the increase in \( C_o \) of the dye (from 4 to 21 mg.L\(^{-1}\)) in both cases of PANI and PANI/SiO\(_2\) composite. At higher concentrations, a large number of dye molecules completely occupy the binding sites of adsorbent materials that were not possible at low dye concentration. Therefore, the \( C_o \) equal to 3. 10\(^{-5}\) mol.L\(^{-1}\) was chosen as the ideal adsorbate concentration for further studies.
Fig. 1 Effect of (a) (b) contact time on the removal of MB by PANI and PANI/SiO$_2$ composite in acidic and alkaline mediums (T=25°C, C$_o$= 3.10$^{-5}$ mol/l, m=0.133 g) c) Effect of the mass of PANI and PANI-SiO$_2$ composite d) Effect of the initial concentration of MB

3.2 Adsorption kinetics

Two kinetic models have been studied in this part, those of pseudo first and second order. The kinetic curves are shown in Figure 2.

The Lagergren's first order pseudo kinetic model (linear form) is expressed by:

\[
\ln (q_e - q_t) = \ln q_e - K_1 t
\]

where $K_1$ is the adsorption rate constant (min$^{-1}$), $q_e$ and $q_t$ are the adsorbed amount of dye in equilibrium and at time t (in mg.g$^{-1}$), respectively [54, 60]. $K_1$, $q_e$ and $R^2$ (correlation coefficient) were obtained graphically and are illustrated in table 1.

As evident in Table 1, $R^2$ values varies from 0.92 to 0.98 for PANI and from 0.80 to 0.85 for PANI/SiO$_2$ in acid and basic medium respectively. As you can see, the (cal. $q_e$) estimated by the
velocity equation is significantly different from the experimental value of \( q_e \) (exp. \( q_e \)). Also, \( R^2 \) value was not very nearby to 1. Therefore, the pseudo first-order model does not fit our experimental data. In addition, the second order pseudo kinetic model (linear form) is expressed by:

\[
t/q_e = (1 / K_2 q_e^2) + (t / q_e)
\]

(3)

where \( K_2 \) is the adsorption rate constant for the pseudo-second order (in g. mg\(^{-1}\). min\(^{-1}\)), \( q_e \) and \( q_t \) were described before. \( K_2 \), \( q_e \) and \( R^2 \) were obtained graphically [61] and are illustrated also in Table 1. The correlation coefficients (\( R^2 \)) of the graphs for various adsorbents vary from 0.99 to 1.00 for PANI in acidic and basic medium and from 0.965 to 0.999 for PANI/SiO\(_2\) in acidic and basic medium, which suggests that adsorption of MB on PANI homopolymer and PANI/SiO\(_2\) composite follows the pseudo-second order model. In addition, \( (q_e, \text{exp}) \) are very close to the \( (q_e, \text{cal}) \).

\[\text{Fig. 2 (a) (b) Pseudo first-order model of PANI and PANI/SiO}_2, \text{ (c) (d) pseudo-second-order model of PANI and PANI/SiO}_2 \text{ kinetic plot for adsorption of MB in acidic and basic mediums.}\]

The intraparticle diffusion model was used to analyze kinetic data of the MB adsorption process, this kinetic model is given by the following equation:
\[ q_t = K_{id} (t)^{0.5} + C \]  \hspace{1cm} (5)

where, \( K_{id} \) and \( C \) are the intraparticle diffusion rate constant and a constant related to the thickness of the boundary layer, these constants are obtained graphically [57, 62, 63]. If the plot is a line, the adsorption of MB is controlled by diffusion resistance. Intraparticle diffusion plots for the adsorption of MB on pure PANI and PANI/SiO\(_2\) composite are illustrated in Figure 3.

\[ q_t = K_{id} (t)^{0.5} + C \]  \hspace{1cm} (5)

The above figure show two stages with different slopes for the polyaniline/SiO\(_2\) composite and for pure polyaniline. The intraparticle diffusion constants (\( K_{id} \) and \( C \)) for all steps are given in Table 1. As evident from the PANI plot, the MB molecules are scattered in adsorbent particles and then spread in their macropores at the beginning of the adsorption process. Subsequently, MB molecules are propagated in polymeric micropores then the equilibrium take place. However, the PANI/SiO\(_2\) plot also involves two steps. This can be explained by the presence of silica nanoparticles and, consequently, to the raise in surface area of the composite. As well illustrated in the first three figures,
the intraparticle diffusion stage is a gradual process. High \( C \) values show that the transfer of additional mass of \( \text{MB} \) molecules on PANI is significant and take place in the beginning of the adsorption process.

### Table 1. Kinetic parameters of adsorption of \( \text{MB} \) on PANI and PANI/SiO\(_2\) in acidic and alkaline mediums.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>PANI pH=2</th>
<th>PANI pH=11</th>
<th>PANI/SiO(_2) pH=2</th>
<th>PANI/SiO(_2) pH=11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 ) (min(^{-1}))</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>-0.03</td>
</tr>
<tr>
<td></td>
<td>( q_e ) (mg/g)</td>
<td>0.22</td>
<td>2.43</td>
<td>2.13</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.921</td>
<td>0.988</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>( K_2 ) (min(^{-1}))</td>
<td>0.48</td>
<td>0.027</td>
<td>0.01</td>
<td>-0.32</td>
</tr>
<tr>
<td></td>
<td>( q_e ) (mg/g)</td>
<td>3.83</td>
<td>4.34</td>
<td>3.61</td>
<td>6.66</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>1.000</td>
<td>0.990</td>
<td>0.965</td>
<td>0.999</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>( K_{id1} )</td>
<td>0.15</td>
<td>0.41</td>
<td>0.63</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>( C_1 )</td>
<td>3.03</td>
<td>0.97</td>
<td>-0.98</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.922</td>
<td>0.99</td>
<td>0.98</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>( K_{id2} )</td>
<td>0.007</td>
<td>0.02</td>
<td>0.068</td>
<td>-0.029</td>
</tr>
<tr>
<td></td>
<td>( C_2 )</td>
<td>3.73</td>
<td>3.80</td>
<td>2.11</td>
<td>6.97</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.999</td>
<td>1.00</td>
<td>0.85</td>
<td>0.76</td>
</tr>
</tbody>
</table>

### 3.3 Adsorption Isotherms

Adsorption isothermal studies are required to apply the adsorption technique for practical purposes. The adsorption mechanism could be determined by evaluating the equilibrium data also known as adsorption data obtained from the experiments. An equilibrium relationship could be established between the amounts of dye adsorbed on the surface of an adsorbent through the adsorption isotherms. In this study, several isothermal models (Langmuir, Freundlich and Dubinin-Radushkevich) were used to examine the adsorption data.

#### 3.3.1 Langmuir Isotherm

The basic assumption of this isotherm is that monolayer formation occurs so that only one dye molecule could be absorbed at an adsorption site and that intermolecular forces decrease with distance. It is also assumed that the surface of the adsorbent has a homogeneous character and has identical and energy equivalent adsorption sites. The Langmuir model is given by the equation below:
\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (7)
\]

Where \( q_m \) is the maximum adsorption amount with full monolayer coverage on the surface of the adsorbent (mg.g\(^{-1}\)) and \( K_L \) is the Langmuir adsorption constant for adsorption energy (L.g\(^{-1}\)) [64], \( C_e \) and \( q_e \) were described before.

The values of \( q_m \) and \( K_L \) can be determined from Figure 4 from the slopes and the interception of the linear curve of \( C_e/q_e \) in function of \( C_e \) and are represented in Table 2 together with \( R^2 \) (correlation coefficient).

![Langmuir Isotherm Plot](image)

**Fig. 4** Langmuir isotherm plot for MB adsorption by (a) (b) PANI and (c) (d) PANI/SiO\(_2\) composite in acidic and basic mediums.

The isotherm is linear for all concentrations range and shows a reasonable adaptation to the adsorption data.

The preference and viability of the adsorption process can be determined by the separation factor \( R_L \) in the data analysis using the Langmuir isotherm. It is given by the equation below:

\[
R_L = \frac{1}{1 + K_L C_0} \quad (8)
\]
If $0 < R_L < 1$ adsorption is favorable, but if $1 < R_L$ adsorption is unfavorable. If $R_L = 0$: adsorption is irreversible and if $R_L = 1$: adsorption is reversible [65]. In this case study, in all the cases: $0 < R_L < 1$ indicating that MB adsorption on PANI and PANI/SiO$_2$ composite is favorable.

3.3.2 Freundlich isotherm

Freundlich's model is applicable to heterogeneous systems and involves the formation of multilayers. This adsorption isotherm is given by:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

(9)

where $k_f$ and $n$ are the Freundlich constants and represent, respectively, the adsorption capacity and the measure of heterogeneity [66]. The values of $k_f$ and $n$ were determined from the linear diagram of $q_e$ in function of $C_e$ (Figure 5) and the values are represented in Table 2.

![Figure 5](image_url)

**Fig. 5** Freundlich isotherm plot for MB adsorption by (a) (b) PANI and (c) (d) PANI/SiO$_2$ composite in acidic and basic mediums.
In this study, n > 1 in all cases, which indicate the favorability of the adsorption process. The data evaluation of the linearly calculated model above sometimes does not provide satisfactory results since linear equations can provide multilinear graphs.

**3.3.3 Dubinin-Kaganer-Radushkevich (DKR) isotherm**

In adsorption studies, the different isotherms studied before are generally used to describe single layer adsorption and cannot determine the mechanisms and energy of adsorption. It is the Dubinin-Kaganer-Radushkevich (DKR) isotherm that can provide the adsorption mechanism and the energy of the adsorption process, which is expressed linearly:

\[
\ln q_e = \ln q_m - B\varepsilon^2
\]

(12)

where \( q_m \) is the theoretical monolayer saturation capacity (mg.g\(^{-1}\)), \( B \) is the constant, called D-R model constant, and \( \varepsilon^2 \) is the Polanyi potential [67], which is determined by the equation:

\[
\varepsilon = RT \log (1+1/C_e)
\]

(13)

where \( R \) is the general gas constant and \( T \) is the absolute temperature [68].

![Dubinin-Kaganer-Radushkevich isotherm plot for MB adsorption by (a) PANI and (c) PANI/\text{SiO}_2 composite in acidic and basic mediums.](image)

**Fig. 6** Dubinin-Kaganer-Radushkevich isotherm plot for MB adsorption by (a) (b) PANI and (c) (d) PANI/SiO\(_2\) composite in acidic and basic mediums.
A comparison of the efficacy of the synthesized materials on the adsorption process is provided in Table 2.

Table 2: Adsorption isotherms parameters of MB adsorption on PANI and PANI/SiO₂ composite at pH 2 and 11.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>PANI (pH2)</th>
<th>PANI (pH11)</th>
<th>PANI/SiO₂ (pH2)</th>
<th>PANI/SiO₂ (pH11)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K&lt;sub&gt;L&lt;/sub&gt; (L g⁻¹)</strong></td>
<td>0.57597</td>
<td>0.09081</td>
<td>1.77328</td>
<td>0.20906</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>q&lt;sub&gt;m&lt;/sub&gt; (mg g⁻¹)</strong></td>
<td>7.89889</td>
<td>13.86385</td>
<td>1.30303</td>
<td>31.42677</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;L&lt;/sub&gt;</strong></td>
<td>0 &lt; R&lt;sub&gt;L&lt;/sub&gt; &lt; 1</td>
<td>0 &lt; R&lt;sub&gt;L&lt;/sub&gt; &lt; 1</td>
<td>0 &lt; R&lt;sub&gt;L&lt;/sub&gt; &lt; 1</td>
<td>0 &lt; R&lt;sub&gt;L&lt;/sub&gt; &lt; 1</td>
</tr>
<tr>
<td><strong>R&lt;sup&gt;2&lt;/sup&gt;</strong></td>
<td>0.88845</td>
<td>0.17234</td>
<td>0.91575</td>
<td>0.3616</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>K&lt;sub&gt;f&lt;/sub&gt; (L g⁻¹)</strong></td>
<td>3.56744</td>
<td>3.92062</td>
<td>0.67684</td>
<td>6.14691</td>
</tr>
<tr>
<td><strong>n&lt;sub&gt;f&lt;/sub&gt;</strong></td>
<td>3.55252</td>
<td>6.6212</td>
<td>3.92572</td>
<td>1.60462</td>
</tr>
<tr>
<td><strong>R&lt;sup&gt;2&lt;/sup&gt;</strong></td>
<td>0.80783</td>
<td>0.08493</td>
<td>0.58776</td>
<td>0.69909</td>
</tr>
<tr>
<td>Dubinin-K-R</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>q&lt;sub&gt;m&lt;/sub&gt;</strong></td>
<td>20.09799</td>
<td>0.0205</td>
<td>1.424 .10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0.00106</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>0.01766</td>
<td>0.09925</td>
<td>0.02045</td>
<td>0.04175</td>
</tr>
<tr>
<td><strong>R&lt;sup&gt;2&lt;/sup&gt;</strong></td>
<td>0.74661</td>
<td>0.85615</td>
<td>0.60007</td>
<td>0.69486</td>
</tr>
</tbody>
</table>

From the literature [67, 68] and the values of q<sub>m</sub> calculated from the linear plot of D-K-R isotherm in figure 6, the process of adsorption in all cases is physical.

3.4 Thermodynamic study:

Thermodynamic parameters, such as E<sub>a</sub> (activation energy), ΔG (Gibb free energy change), ΔH (enthalpy change) and ΔS (entropy change) are useful to explain the nature of adsorption. The E<sub>a</sub> is calculated from the Arrhenius equation, shown below:

\[ k = A \times \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (14)

where T is the absolute temperature, A is the Arrhenius constant and k is the frequency constant [62].

The ΔG is calculated by the following equation [55]:

\[ \Delta G = -RT \ln \frac{q_e}{C_e} \]  \hspace{1cm} (15)
The $\Delta H$ and $\Delta S$ are calculated from the Van't Hoff equation by plotting $\ln \frac{q_e}{C_e}$ vs. $1/T$, as indicated below.

$$\ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (16)

where $T$ is the temperature [69].

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**Fig. 7** Determination of standard enthalpy change for the adsorption of MB by (a) (b) PANI and (c) (d) PANI/SiO$_2$ composite in acidic and basic mediums.

Figure 7 shows the Van’t Hoff diagram, obtained by plotting $\ln q_e/C_e$ vs. $1/T$ after adsorption of MB. The enthalpy change value is useful to explain the adsorption phenomenon. Rehman et al. [70] described the criteria for physisorption and chemisorption between adsorbate and adsorbent in relation with enthalpy change ($\Delta H^\circ$): 4–10 kJ mol$^{-1}$ (physical adsorption), 2–40 kJ mol$^{-1}$ (Hydrogen bonding forces) and $>40$ kJ mol$^{-1}$ (chemical adsorption) [71]. The enthalpy variation values in the present work, as illustrated in Table 3, are -1.21 and +1.37 kJ mol$^{-1}$ for the adsorption of MB on PANI (at pH 2 and 11), -14.1 and +14.56 kJ mol$^{-1}$ for the PANI/SiO$_2$ composite, these values with their negative sign confirm the physical and exothermic process at acidic pH, and endothermic process at alkaline pH.
The $\Delta G$ values are also useful to explain the adsorption phenomenon, explains the spontaneity or non-spontaneity of the adsorption. The $\Delta G$ variation from -20 to 0 kJ mol$^{-1}$ show physisorption and from -400 to -80 kJ mol$^{-1}$ show chemisorption [12, 72]. For the MB adsorption on the pure PANI, The value of $\Delta G^\circ$ varies from -31.22 to -46.10 kJ mol$^{-1}$ and from -22.54 to -47 kJ mol$^{-1}$ for the PANI/SiO$_2$ composite. This result confirms that the process of adsorption between MB and both adsorbents used in this study is physical and spontaneous. The continuous decrease of $\Delta G^\circ$ for the PANI and PANI/SiO$_2$ composite with increasing temperature means that the adsorption became a non-spontaneous process.

**Table 3.** Thermodynamic parameters of adsorption of MB on PANI and PANI/SiO$_2$ composite.

<table>
<thead>
<tr>
<th></th>
<th>T ($^\circ$C)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
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<tr>
<td>PANI</td>
<td>30</td>
<td>-1.21</td>
<td>0.106</td>
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<td></td>
<td>35</td>
<td></td>
<td></td>
<td>$-34.95 &lt; 0$</td>
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<td>40</td>
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<td></td>
<td>45</td>
<td></td>
<td></td>
<td>$-44.03 &lt; 0$</td>
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<td>0.105</td>
<td>$-33.43 &lt; 0$</td>
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<td>$-46.10 &lt; 0$</td>
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<tr>
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<td>0.12</td>
<td>$-22.54 &lt; 0$</td>
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<td>$-26.95 &lt; 0$</td>
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<td>$-47.00 &lt; 0$</td>
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**4. Conclusions**

In the present study, PANI and PANI/SiO$_2$ composite were successfully synthesized and used as adsorbents for removal of MB (cationic dye) from aqueous solutions. The adsorption of MB was studied as a function of contact time, initial MB concentration and sorbent dosing. The general conclusion is that the amount adsorbed using PANI/SiO$_2$ was higher than that with pure PANI. The dye removal rate reaches equilibrium in the 60$^{th}$ minutes with both PANI and PANI/SiO$_2$. A high amount of dye (6.97 mg/g) was adsorbed on PANI/SiO$_2$ composite in comparison to that adsorbed with pure PANI (5.2 mg/g), this is probably due to the presence of high concentration of H$^+$ ions on
the surface of PANI/SiO₂ adsorbent competing with methylene blue (a cationic dye) for adsorption sites in the adsorbent. With an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of adsorbent is lowered. Consequently, removal efficiency is increased. For the PANI, it always exists in the form of ES. This form is rich with the positively charged sites that undergo interaction with anionic moiety of the dye molecule.

By comparing the effect of the medium (acidic or alkaline), the PANI homopolymer and the PANI/SiO₂ composite exhibit high adsorption efficiencies in the alkaline medium compared to those in the acidic medium, this can be explained for PANI/SiO₂ composite by the fact that at low pH values the particles are more and more negatively charged as the pH becomes more and more basic. This is due to the deprotonation of surface silanols (Si-OH) by OH⁻ hydroxyls in solution to form silanolates (SiO⁻). For the PANI, the ES form transforms into the EB form at higher pH. The negative charged surface revealed and the negative charge density increased with the increasing pH value. Therefore, the adsorption capacity increased with the increasing pH value. The 0.133 g of adsorbent mass was selected for all adsorption studies. Therefore, the C₀ equal to 3.10⁻⁵ mol L⁻¹ was chosen as the ideal adsorbate concentration. The pseudo second order is more adequate for the adsorption kinetics of MB by PANI and PANI/SiO₂ composite, with (R²) very important which vary from 0.99 to 1.00 for PANI in acidic and basic medium and from 0.965 to 0.999 for PANI/SiO₂ composite in acidic and basic medium. From the intraparticle diffusion results, the MB molecules are scattered in adsorbent particles and then spread in their macropores at the beginning of the adsorption process. Subsequently, MB molecules are propagated in polymeric micropores then the equilibrium take place. The Langmuir isothermal model fitted more closely to the data of MB adsorption in this study. The enthalpy variation values in the present work, are -1.21 and +1.37 kJ mol⁻¹ for the adsorption of MB on PANI (at pH 2 and 11), -14.1 and +14.56 kJ mol⁻¹ for the PANI/SiO₂ composite, these values with their negative sign confirm the physical and exothermic process at acidic pH, and endothermic process at alkaline pH. The ΔG variation from -31.22 to -46.10 kJ mol⁻¹ for PANI and from -22.54 to -47 kJ mol⁻¹ for the PANI/SiO₂ composite confirms that the process of adsorption between MB and both adsorbents used in this study is physical and spontaneous.
Statements and Declarations

All authors declare that they have no conflict of interest.

References:

[8] T.F. Otero, Conducting polymers: bioinspired intelligent materials and devices (Royal Society of Chemistry, United Kingdom, 2016)


Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- DatasetAdsorptionofMBbyPANIandPANISiO2.xlsx