Adsorption of Azo Dye Onto TiO$_2$ Nanoparticles Prepared by a Novel Green Method: Isotherm and Thermodynamic Study

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Abstract
The current study examined the use of Sansevieria plant leaves extract as an environmentally acceptable, inexpensive, and safe green approach for creating titanium dioxide nanoparticles (NPs). Batch studies have been used to test the particles' capacity to bind to the azo dye congo red (CR), which has been adsorbed from its aqueous solution. The effects of many factors, including the weight of TiO$_2$ NPs, the contact duration to reach equilibrium, the concentration of CR, temperature, and pH, have been investigated. Both the Freundlich and Langmuir models were used to analyze experimental results. According to the high values of the Freundlich model's correlation coefficient $R^2$, it is discovered that the adsorption of CR dye onto nano TiO$_2$ is well-suited. The kinetics analysis for the adsorption trials proposed the pseudo-second-order. Thermodynamic data showed that the CR dye adsorption onto nano TiO$_2$ is a physical process that happens spontaneously and endothermically with increasing unpredictability.

Keywords: Adsorption, azo dye, TiO$_2$ NPs, Isotherm, Thermodynamic, a novel green method.

امتزاز صبغة الآزو على دقائق أوكسيد التيتانيوم النانوية المحضرة بطريقة خضراء جديدة : دراسة متساوي درجة الحرارة والدينمية الحرارية

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الخلاصة
تبحث الدراسة الحالية في استخدام مستخلص أوراق السنسفيرا كطريقة خضراء صديقة للبيئة , رخيصة وغير سامة لتخليق دقائق أوكسيد التيتانيوم النانوية. قابلية امتزاز هذه الدقائق لأمتزاز صبغة الآزو كونغو الحمراء من محاليلها المائية تم إجراءها باستخدام تجارب التجربة . تم دراسة تأثير مختلف الظروف مثل وزن (CR) دقائق أوكسيد التيتانيوم النانوية , زمن الرج , تركيز صبغة الكونغو الحمراء , درجة الحرارة والأس الهيدروجيني . النتائج التجريبيه أظهرت تطبيقاً إلى إنموذج فرندلش وفترش . لقد وجد أن امتزاز صبغة الكونغو الحمراء على سطح أوكسيد التيتانيوم النانوي جيد التوافق مع إنموذج فرندلش طبقاً الى قيمة معامل الأرتباط $R^2$ العالية.

الدراسة الحركية لتجارب الأمتزاز متفرج كون عملية الأمتزاز تتبع المركبة الثانية المتميزة , النتائج الترمودينميكية

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1- Introduction

Wastewater is a significant contributor to environmental pollution since it is a byproduct of the use of water in homes, companies, and enterprises [1]. Since a lot of dye waste is dumped into rivers, causing significant environmental harm, dyes are a substantial source of water pollution [2]. The decolourization of the dyes in industrial wastewater involved various techniques. These techniques of treatment consist of ultrafiltration [3], ion-exchange [4], electro-chemical-degradation [5], photo catalytic degradation [6, 7] and adsorption process [8]. The adsorption of dye onto nanoparticles was the most practical approach since it is straightforward, highly efficient, and can use a variety of materials as adsorbents [9]. Adsorption refers to a solid's capacity to accumulate other substances from solution on its surfaces. Many materials have been employed as adsorbents for decolorizing industrial wastewater, including raw with activated illite mixed, chlorite and kaolinite [10], modified bentonite [11] and Thuja plant [12]. TiO$_2$ nanomaterials are now regarded as a promising material that is heavily involved in getting rid of toxic organic containments through the adsorption and photo-catalytic process due to the stability of its structure, bio-compatibility, strong oxidizing agent, [13] and non-toxicity of the metal precursors [14-19]. TiO$_2$ nanoparticles were previously used frequently for the treatment of textile effluents. TiO$_2$ nanoparticles are produced using a variety of techniques, including biosynthesis, sol-gel process, and plasma-enhanced chemical vapour deposition (PE-CVD). TiO$_2$ nanoparticle biosynthesis is receiving a lot of attention due to its ease of usage, low cost, and lack of toxicity [20]. As a result, plant and herbal extracts are increasingly appealing due to the easier and more cost-effective process and the inclusion of ingredients including flavonoids, terpenoids, and polysaccharides [21].

The objectives of this work was to synthesize TiO$_2$ nanoparticles utilizing a unique biosynthesis technique based on a leaf extract from the Sansevieria plant. Additionally, this study assessed the efficiency of these synthesized nanomaterials to adsorb CR dye from solution. The effects of several variables, including the weight of TiO$_2$ NPs, the contact time required to reach equilibrium, the initial concentration of CR, temperature, and pH, were investigated. To comprehend the mechanism of the adsorption process, kinetic, thermodynamic, and adsorption isotherm models were studied.

2. Experimental part

2.1. Materials

**Adsorbent:** Titanium dioxide nanoparticles were synthesized using an extract from Sansevieria plant leaves, which were bought from a local market. The leaves of this plant were cut, thoroughly washed with tap water, and then repeatedly cleaned with D.W. to get rid of any remaining dust and grime. A 100 mL of boiling, distilled water was combined with 25 g of finely chopped plant material, and the mixture was continually heated for 2 hours at 90 °C. Using No. 1 filter paper, the plant extract was filtered. A 2.8 mL of titanium tetrachloride was added to 100 mL of distilled water as a precursor, and the mixture was well agitated. The previously produced Sansevieria plant leaf extract was gradually added to the titanium tetrachloride solution while being continuously stirred. For four hours, the mixture was continually stirred. The precipitate was regularly calcined at 500 °C for 4 hours after being dried at 100 °C for 24 hours. The precipitate will be rinsed with D,W many times to remove the contaminants. The titanium dioxide nanoparticles were then obtained as a white precipitate after being heated at 700 oC for an hour. The precipitate was then crushed in a lab mill and kept in a
dry area. Utilizing XRD (XRD, PW1730, Philips, Holanda) analysis, the synthesized TiO$_2$ was identified. The data collected for TiO$_2$ powder showed that the average crystalline size was 15.2 nm. Atomic force microscopy AFM (Nano AFM 2022, Nanosurf, Switzerland) measurements indicated that TiO$_2$ sample has a small size distribution with a diameter of 67.73 nm. TiO$_2$-NPs were investigated by FTIR spectroscopy (Shimadzu IR-Affinity-1 Japan). The metal-oxygen bonding is confirmed by the peaks that are characteristic of the Ti-O bending mode of vibration, which has a center frequency of 497.63 and 688.59 cm$^{-1}$. The Ti-O stretching bands are described by the sharp peak between 800 and 450 cm$^{-1}$. The morphology of the prepared TiO$_2$ was detected by scanning electron microscopy SEM using (FESEM-EDS, MIRA III, TESCAN, Czech), the particle size of TiO$_2$-NPs was found to be 42.039 nm. Figure 1 shows the steps of TiO$_2$ NPs preparation [22].

**Figure 1:** Steps used for synthesis of TiO$_2$ NPs using Sansevieria plant leaves.

**Adsorbate:**
Congo red (CR), an anionic dye or acidic dye, with a molar mass of 696.665 g/mole and the chemical formula C$_{32}$H$_{22}$N$_6$Na$_2$O$_6$S$_2$. Disodium 4-amino-3-[4-[4-[1-amino-4-sulfonanaphthalene-2-yl] diaziny]-phenyl]phenyl]diaziny]-naphthalene-1-sulonate is the compound's IUPAC nomenclature. The highest absorption of this dye is 497 nm, making it useful as a substitute indicator to mimic contamination in industrial wastewater [23]. The chemical structure of this dye is shown in Figure 2.
2.2. Adsorbate preparation:

One gram of the CR dye was diluted with one liter of distilled water to prepare the stock solution. To prepare different CR dye concentrations, 10, 20, 30, 40, and 50 mg/L, the stock solution was further diluted. The absorbance of each solution is measured using UV-Vis spectrophotometer (Shimadzu UV-1800) Japan.

2.3. Adsorption Experiments:

Using the batch equilibrium approach, adsorption experiments were conducted. In a 25 mL CR solution that was placed in a 100 mL conical flask, a specific weight of TiO₂ NPs sample was added. Then, the mixture was shaken with a thermostatic water bath of the JTYS-1000 design from China at a speed of 150 rpm for 60 minutes at various temperatures. The residual CR dye concentration was determined using a Shimadzu UV-1800 UV-Vis Spectrophotometer after 10 minutes of centrifugation at 4000 rpm to separate the adsorbent.

The removal percentage (R%) for CR and the amount of the adsorbed dye (qe) in mg.g⁻¹ were estimated as the following relations [24]:

\[ R\% = \left[ \frac{C_i - C_e}{C_i} \right] 100 \]  \hspace{1cm} (1)

\[ q_e = \frac{V}{w} \left[ C_i - C_e \right] \]  \hspace{1cm} (2)

Cᵢ, Cₑ are the initial concentration and the equilibrium concentration mg/L, V is the working solution volume (L) and w is the weight of TiO₂ NPs sample (g). The kinetics study for the adsorption of CR on TiO₂ NPs was carried out using 25 mL of 10 mg/L CR dye solution under the following conditions: the adsorption time (10, 20, 30, 40, 50, 60) minutes, pH equals to 7, shaking speed 150 rpm at five different temperatures of (288 to 328) K, in a set of 100 mL conical flasks. A 1.0 mL of the supernatant was taken out every five, ten, twenty, thirty, forty, fifty, and sixty minutes until the dye reached equilibrium. At a speed of 4000 rpm, the liquid and solid phases were separated for five minutes. The supernatant was analyzed to determine the adsorbate concentration using UV-Vis spectrophotometer (Shimadzu UV-1800) Japan.

3. Results and Discussions

3.1. Impact of TiO₂ NPs weight

Various amounts of TiO₂ NPs in the range of (0.05 to 0.3) g and 25 mL of 10 mg/L CR dye were used in experiments to determine the effect of the TiO₂ NPs weight on the removal % of the CR dye. The conditions were 298 K, pH = 7, and 150 rpm shaking. According to Figure 3, when the weight of TiO₂ NPs increased, the R% for CR dye increased from 39.09 to 96.10%.
The availability of more adsorption sites for CR dye was increased by the elevation in R% values [25]. As a consequence, 0.2 g is selected as the optimum mass for further studies with the help of the prior finding.

**Figure 3:** Effect of TiO$_2$ NPs weight on the R% of CR dye.

### 3.2. Effect of contact time

The effect of altering the CR dye adsorption duration from 5 to 80 minutes was determined while maintaining other parameters such pH 7, starting CR concentration of 10 mg/L, TiO$_2$ NPs weight of 0.2 g, and 150 rpm shaking speed at 298 K. The effects of agitation time on the adsorption of CR dye are shown in Figure 4. The proportion of removal in this figure increases with passing time and reaches equilibrium in around 60 minutes, after which the rate of removal remains constant. This might be a reference to the possibility of CR molecules adhering to a wide surface area on all adsorbents for at least 60 minutes after the unoccupied surface sites have been saturated, because of this, the removal efficiency is unaffected. Thus, 60 minutes was chosen as the optimum time period.

**Figure 4:** Effect of contacting time on the adsorption of CR dye on TiO$_2$ NPs.

### 3.3. Effect of initial concentration on the adsorption process
The impact of starting CR concentration on the adsorption were experimentally examined at CR concentration ranging (10, 20, 30, 40, and 50) mg/L, TiO$_2$ NPs weight under following experimental conditions: 0.2 g, pH equals to 7, at 298K , contact time 60 minutes and 150 rpm of shaking speed. The values of the adsorption dye q$_e$ (mg/g) increased from (1.246 to 4.838) mg/g when the CR concentration increased, according to Figure 5a. This was linked to a significant probability of dye molecule collision with surfaces of TiO$_2$ NPs, together with a high rate of dye diffusion onto adsorbent surface [26]. Further, Figure 5b demonstrates that when beginning CR concentration increased, the R% for CR fell from (93.92 to 56.79)%. The increased absorption of CR dye at low concentrations suggests the potential of more binding sites on the surface of TiO$_2$ NPs for less CR, which may be connected to the lack of viable binding sites necessary for the high beginning CR concentration [27]. Figure 5a shows the relation between the starting CR concentration and the adsorption amount q$_e$.

**Figure 5:** Effect of initial concentration of CR on the adsorption of CR dye on TiO$_2$ NPs. (a) Adsorption capacity q$_e$ (mg/g). (b) Removal efficiency R%.

### 3.4. Effect of temperature on adsorption of CR dye on TiO$_2$ NPs

By adjusting the temperature from (288 K to 328 K), it was possible to determine the percentage of CR dye that was removed using TiO$_2$ NPs samples. The studies involved mixing 25 mL of 10 mg/L CR solutions with 0.2 g of TiO$_2$ NPs for 60 minutes at a speed of 150 rpm. The effect of temperature on CR dye adsorption on TiO$_2$ NPs is shown in Figure 6. This Figure demonstrates that raising the temperature from (288 K to 328 K) causes the percentage removal
to grow before stabilizing at a constant value, which is why the adsorption process has been categorized as an endothermic process [28]. This can be because the sorption process occurred.

![Figure 6: Effect of temperature on the adsorption of CR on TiO$_2$ NPs.](image)

**3.5. pH effect**

The removal of CR using a sample of TiO$_2$ NPs is examined in the pH range of (2.6-10.8) at 298 K, initial CR concentration of 10 mg/L, 0.2 g weight of TiO$_2$ NPs, 60 min of shaking time and 150 rpm of shaking speed. Figure 7 shows that the amount of CR dye removed by TiO$_2$ NPs has decreased from (97 to 58)% when the pH values changed from (2.6 to 10.8). This can be explained by the following fact due to the high positive charge density on the adsorbent's surface, the adsorption of the anionic CR dye can be increased in an acidic media. When the pH is lower, the increase in H$^+$ concentration in TiO$_2$ NPs generates a positive charge through H$^+$ adsorption, which causes the adsorption of CR dye to increase. Since TiO$_2$ NPs are positively charged in an acidic environment, they exhibit a high electrostatic attraction to CR anions, leading to the maximal elimination of the CR dye. While this is happening, the number of negatively charged sites that are unfavorable for the adsorption of CR dye molecules due to electrostatic repulsion is expanding as pH values increase [29].

![Figure 7: Effect of pH on the adsorption of CR dye on TiO$_2$ NPs.](image)

**3.6. Adsorption Isotherm Models**
To describe the type of interaction and equilibrium relationship between the TiO$_2$ NPs surface and CR dye molecules, the isotherm models is applied [30].

### 3.6.1. Langmuir isotherm model:

Based on the formation of uniform and a homogenous sites for adsorption, Langmuir linear forms is presented by following the equation [31]:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e$$

Where $C_e$ CR equilibrium concentration mg/L, $q_e$ amount of the adsorbate that adsorbed per g of the adsorbent at equilibrium mg/g, $Q_m$ maximum adsorption capacity of the monolayer coverage mg/g and $K_L$ Langmuir isotherm constant L.mg$^{-1}$. The calculated parameters are listed in Table 1.

Where the values of $Q_m$ and $K_L$ are estimated from the slope and intercept of the line obtained from drawing $C_e/q_e$ versus $C_e$ as shown in Figure 8. The fundamental characteristic can also be indicated by Langmuir's equation in terms of a dimensionless constant, $R_s$ is the separation factor expressed as:

$$R_s = 1 / (1 + K_L C_i)$$

Where $C_i$ is the initial concentration (mg.L$^{-1}$). The $R_s$ values suggested the shape of the isotherm to be either linear $R_s=1$, favorable $0 < R_s < 1$, unfavorable $R_s > 1$ or irreversible $R_s = 0$ [32]. The obtained values are given in Table 1. The $R_s$ values are less than one and greater than zero show a favorable adsorption.

![Figure 8: Langmuir isotherms of CR dye on TiO$_2$ NPs at various temperatures.](image)

### Table 1: Langmuir constants data for adsorption of CR dye on TiO$_2$ NPs at various temperatures.
3.6.2. Freundlich isotherm:

This model deals with multilayer, non-ideal, reversible adsorption onto heterogeneous energy surface system [30]. The linear form of this model can be expressed as [33]

\[
\ln q_e = \ln K_{Fr} + \left( \frac{1}{n_f} \right) \ln C_e
\]  

(5)

Where: \( C_e \) (mg/L) is the equilibrium concentration, \( K_{Fr} \) is Freundlich constant indicated to adsorption capacity, and \( n_f \) constant that depended on the temperature and the adsorbate nature. The values of \( K_{Fr} \) and \( n_f \) can be estimated from the linear plot \( \ln q_e \) versus \( \ln C_e \) as shown in Figure 9. These values are listed in Table 2. When \( \frac{1}{n_f} \) equals to 1, the curve of the adsorption is linear which indicates no interaction between the CR species and the adsorbent sites. While when \( \frac{1}{n_f} \) greater than 1, the adsorption is not favorable, the adsorption capacity decreases and the bonds of adsorption become weak. Whereas, \( \frac{1}{n_f} \) less than 1 the adsorption capacity shows an increase and the adsorption is then favorable [34].

![Figure 9](image)

**Figure 9:** Freundlich isotherm plot for the adsorption of CR on TiO\(_2\) NPs at various temperatures.

**Table 2:** The values of Freundlich isotherm data at various temperatures for the adsorption of CR dye on TiO\(_2\) NPs.
3.7. Thermodynamic Study:

Thermodynamic data such as Gibbs free energy $\Delta G^\circ$, standard enthalpy changes $\Delta H^\circ$ and standard entropy changes $\Delta S^\circ$ were estimated using the following equations:

$$
\Delta G^\circ = -RT\ln K_{eq}
$$

$$
K_{eq} = \frac{C_i - C_e}{C_e} [V/m]
$$

$$
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
$$

Where: $K_{eq}$ is the equilibrium constant for the adsorption process, $R$: is the universal gas constant, $T$: absolute temperature (K), $C_i$ and $C_e$: are the initial and the equilibrium concentrations (mg/L) of the adsorbate, respectively, $V$: is the CR solution’s volume (L) and $m$: is the mass of the TiO$_2$ NPs (g). The standard entropy $\Delta S^\circ$ and enthalpy $\Delta H^\circ$ can be calculated from the intercept and the slope of the line between $\ln K_{eq}$ versus $1/T$ using Van’t Hoff equation [35]: as shown in Figure 10:

$$
\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
$$

Values of the thermodynamic data are given in Table 3. At all temperatures, the values of $\Delta G^\circ$ are negative and it become more negative when the temperature has increased. This finding suggested that at high temperature the adsorption of CR onto TiO$_2$ NPs being more spontaneous. While the positive values of $\Delta S^\circ$ and $\Delta H^\circ$ give an indication that this process endothermic accompanied with increase in the disorder [36]. Since the values of $\Delta G^\circ$ less than 20 kJmol$^{-1}$, it can be predicted that the adsorption process followed physisorption type [37].
Figure 10: Van’t Hoff plots for the adsorption of CR dye on TiO$_2$ NPs.

Table 3: Thermodynamic parameters for the adsorption of CR dye on TiO$_2$ NPs.

<table>
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<th>$C_i$ (mg/L)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol)</th>
<th>(-) $\Delta G^\circ$ (kJ/mol)</th>
<th>288K</th>
<th>298K</th>
<th>308K</th>
<th>318K</th>
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3.8. Kinetics of Adsorption:

In this study, two different kinetic models: Pseudo first order (PFO) and Pseudo second order (PSO) have been applied. The linearized PFO and PSO models written respectively as equations [38]:

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

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

Where $q_t$, $q_e$ are the amount of CR dye molecules adsorbed on the TiO$_2$ NPs at time $t$ and at equilibrium (mg/g). $k_1$ (min$^{-1}$), $k_2$ (g.mg$^{-1}$.min$^{-1}$) are the rate constants of PFO and PSO respectively. The linear plot of $\ln (q_e - q_t)$ versus ($t$) and $t/q_t$ versus $t$ are employed to calculate $k_1$, $q_e$ values for PFO and $k_2$, $q_e$ for PSO as shown in Figures 11 and 12. Table 4 lists the PFO and PSO constants for the adsorption process. As shown in Table 4, the values of correlation coefficient $R^2$ for PSO were higher than that for PFO also, the values of $q_e$ experimental $q_{e,exp}$ and $q_e$ calculated $q_{e,cal}$ were matched well using PSO kinetic models, suggesting that the mechanisms of the adsorption related to the both adsorbent and adsorbate [39].

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Figure 11: PFO plot of kinetics of CR dye on TiO\textsubscript{2} NPs at various temperatures.

Figure 12: PSO plot for the adsorption of CR on TiO\textsubscript{2} NPs at various temperatures.

Table 4. PFO and PSO kinetics data for adsorption of CR dye on TiO\textsubscript{2} NPs at various temperatures.

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<th>T (K)</th>
<th>( q_{e \text{ exp}} ) (mg/g)</th>
<th>( q_{e \text{ cal}} ) (mg/g)</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( q_{e \text{ exp}} ) (mg.g(^{-1}))</th>
<th>( q_{e \text{ cal}} ) (mg.g(^{-1}))</th>
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Conclusion
From this study, it can be observed that CR dye may be effectively removed from its aqueous medium utilizing TiO\textsubscript{2} NPs that were synthesized using Sansevieria plant leaves extract. The Freundlich isotherm was the most effective model for the data at equilibrium. PSO model served as a better representation of the kinetic investigation. The adsorption of CR onto TiO\textsubscript{2} NPs was physisorption, endothermic and it spontaneously occurs as the randomization increases.
References


