Adsorption of safranin dye from their aqueous solutions by using CA and Nano FeO/CA

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Abstract The safranin dye adsorption from the surface of Nano Iron oxide, using UV-visible spectroscopy device. The effect of temperature within the range (328-298) Kelvin. In the adsorption, process of safranin dye was investigated. The results showed that the adsorption increased with increasing temperature, i.e. the reaction is endothermic (adsorption and absorption). Dye removal was (R% = 97.691) at acid medium. This study indicated the susceptibility of Nano Iron oxide (Nano FeO/CA) in removing safranin dye with a high efficiency of aqueous solution. The material Nano FeO / CA had a better adsorption capacity than CA at concentration of (5) ppm of the dye and was (1.910 mg / g).

Keywords. Activated carbon, Nano Iron oxide, Dyes, Adsorption and UV-visible spectroscopy.

1. Introduction
Environmental pollution is a problem of main concern in several countries[1]. However, water pollution shows the main environmental pollution in various countries[2]. Water pollution have a negative effect on human health [3]. The contamination color in the effluent is the big problem of the environment, and it is important to treat such as this contaminant[4]. Dyes are used in many industries, including the textile, paper, and leather industries[5]. Dyes have complex structures and synthetic origin and difficult to Decompose into the water[6]. Related, some dyes effect on human health such as Disturbance in liver, brain , kidney and considered carcinogens and toxic[7]. Also, dyes have negative effect on aquatic life, because it can reduce the efficiency of photosynthesis in water plant, and effect on their growth. Safranin dye is one of the known industrial dyes, and it is one of the oldest dyes used[8]. The molecular formula for this dye is (C₂₀H₁₉N₄Cl ) and this dye has several names such as (basic red 2) and (Safranin O)[9]. This dye also has the ability to dissolve in water and the greatest wavelength of it (520 nm)[10]. This dye is included in many Among the industries at the present time, including in the paper, textile and silk industries as well, this dye is used to dye food and dessert coloring, despite the benefits of this dye, but when discharge to the water it causes water pollution and affects human health[11].

There are many techniques for removing dyes from water and the adsorption is one of most important technology. Adsorption technology is used to remove dyes from water because it is simple to operate, cheap and highly efficient [12]. Recently, adsorbent the activated carbon by adsorption technology is become widely using in the separation processes. Activated carbon have large surface area and abundance which preferably to use as a sorbent to remove dyes[13].
In the last few years, the use of Nano-iron oxide began to remove dyes from water due to its good qualities, which are high-efficiency, cheap and abundant, and Nano-iron oxide is used in many applications, including in medicine and chemistry, and in industrial water treatment and other applications.[14]

This research aims to use activated carbon and Nano Iron oxide as an adsorbent substance to remove Safranin dye from the wastewater through the adsorption process. In addition, study the factors affecting adsorption (temperature, time, pH, adsorption capacity).

2. Material and Methods

2.1. Determine The greatest wavelength ($\lambda_{max}$) for Safranin dye
To determine the maximum wavelength of the Safranin dye, at which the maximum absorption occurs, UV-visible spectrometer device is used within the range (200-800nm) when using a quartz cell with a section length of (1cm) where the appropriate concentration is taken for the dye.

2.2. Determine calibration curve for Safranin dye
To set the calibration curve, six different concentrations were prepared (10-1-0.1-5-0.5-0.05) ppm from Safranin dye, and then its absorbance of These concentrations were measured at the maximum wavelength of the dye, then the calibration curve was drawn between the absorbance and concentration and (Least squares method) was used as a method to treat absorption values statistically.

2.3. Determination of adsorption capacity
Four different weights were taken from the activated carbon (CA) and also from the substance Nano FeO / CA (0.1,0.05, 0.025,0.075) gm. Two primary concentrations were selected from the safranin dye (5) and (0.5) ppm in size (10) ml. Related, the 10 ml of solution was added separately to each of the activated carbon weights and the Nano FeO / CA weights with continuous stirring of the solution for a (10) minutes. The solution was filtered by the filter paper, and then the absorbance of the remaining filter was measured.

2.4. Determine the pH for adsorption
The pH of the safranin dye were taken at (1, 3, 5, 7, 9, 11) and an initial concentration of the dye (5) ppm was chosen in size (10) ml. Meanwhile, a few drops of acids or diluted bases were added to a solution according to the need, which is (HCl), (CH₃COOH) (NaOH), (NH₄OH). The pH of the solution was measured using a pH-meter. The activated carbon was added with the substance of Nano FeO / CA at weight 0.025 (gm) separately to the solution. At the same time, the solution was shaken for 10 minutes. The solution was filtered with filter paper and then the absorbance was taken in different stage of the PH.

2.5. Determination of shaking time for adsorption
To determine the shaking time for safranin dye were taken at (120,90,60,50,40,30,20,15,10,5) minutes and was chosen an initial concentration of dye (5) ppm in size (10) ml. pH was set at (pH = 1).The (0.025) weight from (CA) and the Nano FeO / CA gm was added to the dye solution separately. The solution was shaken in different times and then solution was filtered with the filter paper, then absorbance was measured in different times.

2.6. Determine the temperature of the adsorption process
The effect of temperature on the adsorption process was investigated. For determination the temperature of adsorption, the experiments were carried out specific values of temperature and the values were (298,308,318,328) Kelvin, where an initial concentration of the dye at (5) ppm in size (10) ml. Additionally, the acid function was prepared at (pH = 1) within Shake the solution for (10) minutes. Take (0.025) g from (CA) as well as Nano FeO / CA separately. Finally, the solution was put in the
water bath device and calculated from different temperature values. Measure the absorbance of the solution after filtering stage for the solution within filter paper.

3. Results and Discussions

3.1. Adsorption of Safranin dye

3.1.1. Calibration curve for Safranin dye

Figure (1) shows the calibration curve for Safranin dye using the single-spectrum ultraviolet and visible spectroscopy, after the maximum wavelength for the Safranin dye was determined using the two-beam UV and visible spectroscopy at (520 nm), Where different dye concentrations were measured (10-0.05) ppm at this wavelength, and the absorption values of the dye were statistically treated using the Least squares method and it was found that:

\[ Y = 0.0641X + 0.0146 \]

\[ R^2 = 0.9996 \]

\[ [\text{Safranin}] = \frac{\text{Abs.} - \text{Intercept}}{\text{Slope}} \]

Figure 1: Calibration curve for Safranin dye Chemical Properties

3.1.2. Calculation of adsorption capacity for Safranin dye

Table (1) and Figure (2) show calculation of adsorption capacity of Safranin dye using CA and Nano FeO / CA as adsorbents for this dye. Concentrations were determined by measuring the absorbance at the greatest wavelength for dye Safranin and which is (520 nm) by ultraviolet and visible single-spectrum.

| [Safranin]₀ ppm | V, L | Wt, g | Abs. | [Safranin]ᵣ ppm | Cₛₒₐₐₐ ppm | Qᵣ mg/g | Wt, g | Abs. | [Safranin]ᵣ ppm | Cₛₒₐₐₐ ppm | Qᵣ mg/g |
|-----------------|------|-------|------|------------------|-------------|----------|------|------|------------------|-------------|----------|
| 5               | 0.01 | 0.1   | 0.049| 0.536            | 4.463       | 0.446    | 0.1  | 0.038| 0.365            | 4.634       | 0.463    |
| 5               | 0.01 | 0.075 | 0.048| 0.521            | 4.478       | 0.597    | 0.075| 0.036| 0.333            | 4.666       | 0.622    |
| 5               | 0.01 | 0.05  | 0.045| 0.474            | 4.525       | 0.905    | 0.05 | 0.032| 0.271            | 4.728       | 0.945    |
| 5               | 0.01 | 0.025 | 0.042| 0.427            | 4.572       | 1.829    | 0.025| 0.029| 0.224            | 4.775       | 1.910    |
| 0.5             | 0.01 | 0.1   | 0.022| 0.115            | 0.384       | 0.038    | 0.1  | 0.018| 0.053            | 0.446       | 0.044    |
| 0.5             | 0.01 | 0.075 | 0.021| 0.099            | 0.400       | 0.053    | 0.075| 0.017| 0.037            | 0.462       | 0.061    |
| 0.5             | 0.01 | 0.05  | 0.02  | 0.084           | 0.415       | 0.083    | 0.05 | 0.016| 0.021            | 0.478       | 0.095    |
| 0.5             | 0.01 | 0.025 | 0.019| 0.068            | 0.431       | 0.172    | 0.025| 0.015| 0.006            | 0.493       | 0.197    |
Figure 2: adsorption capacity for Safranin dye

From the note of Table (1) and Figure (2), We find that the highest adsorption value was at the Nano-iron oxide with an adsorption capacity (1.910 mg/g) while the active carbon had the highest adsorption capacity (0.536 mg/g) at the concentration of (5) ppm, and the lowest adsorption capacity of the Nano-iron oxide was (0.044 mg/g) and for the activated carbon it was (0.068 mg/g) at a concentration (0.5) ppm, where the adsorption increases With weight loss, and adsorption decreases with weight gain, and this is in agreement with [15].

3.1.3. Effect of the pH on the Safranin dye adsorption percentage value

Table (2) and Figure (3) show the effect of the pH on the adsorption of Safranin dye using CA and Nano FeO / CA as adsorbents for this dye. Where an initial concentration was chosen from the dye (5) ppm, with a volume of (10) ml, and the remaining concentrations were determined at different acidic function. (pH = 11-1) by measuring the absorbance at the greatest wavelength of Safranin dye (520 nm) and then calculating the percentage of removal.

| pH, ppm | [Safranin]o, ppm | V, L | Wt, g | Abs. | [Safranin]f, ppm | R% | Wt, g | Abs. | [Safranin]f, ppm | C_Solid, ppm | R% |
|--------|-----------------|-----|-------|------|-----------------|---|-------|------|-----------------|-------------|---|
| 1      | 5               | 0.01| 0.025 | 0.035| 0.318           | 4.681 | 93.634 | 0.025 | 0.022           | 0.115       | 4.884 | 97.691 |
| 3      | 5               | 0.01| 0.025 | 0.037| 0.349           | 4.650 | 93.010 | 0.025 | 0.024           | 0.146       | 4.853 | 97.067 |
| 5      | 5               | 0.01| 0.025 | 0.04  | 0.396           | 4.603 | 92.074 | 0.025 | 0.027           | 0.193       | 4.806 | 96.131 |
| 7      | 5               | 0.01| 0.025 | 0.042| 0.427           | 4.572 | 91.450 | 0.025 | 0.029           | 0.224       | 4.775 | 95.507 |
| 9      | 5               | 0.01| 0.025 | 0.047| 0.505           | 4.494 | 89.890 | 0.025 | 0.032           | 0.271       | 4.728 | 94.570 |
| 11     | 5               | 0.01| 0.025 | 0.053| 0.599           | 4.400 | 88.018 | 0.025 | 0.038           | 0.365       | 4.634 | 92.698 |
Effect of pH on adsorption of Safranin dye

From the note of Table (2) and Figure (3), we find that the highest dye removal rate was for Nano-iron oxide (R%=97.691) at the acid function (pH=1), while the highest percentage removal for activated carbon is (R%=93.634) at the same acidic function, and the lowest dye removal rate for Nano-iron oxide was (R%=92.698) at the acid function (pH=11). The lowest removal rate for activated carbon was (R%=88.018) at the same acidic function, where we note that adsorption increases at the higher acidic medium and adsorption decreases at the basal medium and this is in agreement with [16].

3.1.4. Effect of shaking time on the adsorption process for Safranin dye

Table (3) and Figure (4) show the effect of shaking time on the adsorption of Safranin dye using CA and Nano FeO / CA as adsorbents for this dye. Where an initial concentration was chosen from the dye (5) ppm with a volume of (10) ml, adjusting the acid function at (pH = 1) and the weight of the adsorption materials used (0.025) g separately for conducting removal experiments. The remaining concentrations were determined at different times of shaking time (5-120) minutes by measuring the absorbance at the maximum wavelength of Safranin dye (520 nm) and then calculating the percentage of removal.

Table 3. Effect of shaking time on adsorption of Safranin dye using CA and Nano FeO / CA

| Time, min. | [Safranin]o ppm | V, L | Wt, g | Abs. | [Safranin]f ppm | Csolid ppm | R% | Wt, g | Abs. | [Safranin]f ppm | Csolid ppm | R% |
|-----------|-----------------|-----|-------|------|-----------------|------------|-----|-------|------|-----------------|------------|-----|
| 5         | 5               | 0.01| 0.025 | 0.036| 0.333           | 4.666      | 93.322| 0.025 | 0.023 | 0.131           | 4.868      | 97.379|
| 10        | 5               | 0.01| 0.025 | 0.03 | 0.240           | 4.759      | 95.195| 0.025 | 0.018 | 0.053           | 4.946      | 98.939|
| 15        | 5               | 0.01| 0.025 | 0.039| 0.380           | 4.619      | 92.386| 0.025 | 0.024 | 0.146           | 4.853      | 97.067|
| 20        | 5               | 0.01| 0.025 | 0.043| 0.443           | 4.556      | 91.138| 0.025 | 0.025 | 0.162           | 4.837      | 96.755|
| 30        | 5               | 0.01| 0.025 | 0.049| 0.536           | 4.463      | 89.266| 0.025 | 0.027 | 0.193           | 4.806      | 96.131|
| 40        | 5               | 0.01| 0.025 | 0.054| 0.614           | 4.385      | 87.706| 0.025 | 0.028 | 0.209           | 4.790      | 95.819|
| 50        | 5               | 0.01| 0.025 | 0.056| 0.645           | 4.354      | 87.082| 0.025 | 0.03 | 0.240           | 4.759      | 95.195|
| 60        | 5               | 0.01| 0.025 | 0.059| 0.692           | 4.307      | 86.146| 0.025 | 0.031 | 0.255           | 4.744      | 94.882|
| 90        | 5               | 0.01| 0.025 | 0.063| 0.755           | 4.244      | 84.898| 0.025 | 0.033 | 0.287           | 4.712      | 94.258|
| 120       | 5               | 0.01| 0.025 | 0.067| 0.817           | 4.182      | 83.650| 0.025 | 0.034 | 0.302           | 4.697      | 93.946|
From the note of Table (3) and Figure (4), we find that the highest adsorption percentage for Nano-iron oxide was (R% = 98.939) at the time of shaking (10 min), while the highest adsorption percentage for activated carbon was (R% = 95.195) at the same shaking time, and the lowest adsorption percentage for Nano-iron oxide was (R% = 93.946) at shaking time (120 min), while the lowest adsorption percentage for active carbon was (R% = 83.650) at the same time as shaking, and it was found that adsorption decreases with increasing time, and this is in agreement with [17].

3.1.5. Study the effect of temperature and the calculation of some thermodynamic functions of the Safranin dye adsorption process

Table (4) shows the effect of temperature on adsorption of Safranin dye using CA and Nano FeO / CA as adsorbents for this dye. Where an initial concentration was chosen from the dye (5) ppm, size (10) ml, adjusting the acid function at (pH = 1), shaking time (10) minutes, and the weight of the adsorbent materials used (0.025) g separately, to perform removal experiments. The remaining concentrations were determined at different temperatures (298-328) K by measuring the absorbance at the greatest wavelength of Safranin dye (520 nm) and then calculating the percentage of removal. Also, some thermodynamic functions were determined and calculated by drawing the relationship between logKd vs. 1 / T using the Fant Hove equation and finding the tendency and reliance on the mathematical and statistical equations for CA and Nano FeO / CA as shown in Figures (5) and (6), respectively.
Figure 6. Effect of temperature on adsorption of Safranin dye using Nano FeO / CA
Table 4. Effect of temperature and calculation of some thermodynamic functions for the adsorption process Safranin dye using CA and Nano FeO / CA

| un | V, L | W, g | Abs. | [Safranin] ppm | C_{total} ppm | R% | K_d | logK_d | ΔH, KJ/mol | ΔG, KJ/mol | ΔS, KJ/mol | K_d | logK_d | ΔH, KJ/mol | ΔG, KJ/mol | ΔS, KJ/mol |
|----|------|------|------|--------------|--------------|-----|-----|--------|-------------|------------|------------|-----|--------|-------------|------------|------------|
| 0.0 | 0.02 | 0.03 | 2    | 0.271        | 4.72         | 94.57| 338.28| 2.577  | -14.708     | 0.02       | 0.084      | 4.91  | 5      | 98.31        | 393.26     | 0.084      |
| 1   | 0.02 | 0.03 | 1    | 0.255        | 4.74         | 94.88| 379.53| 2.579  | -15.210     | 0.02       | 0.068      | 4.93  | 1      | 98.82        | 394.50     | 0.068      |
| 0.0 | 0.02 | 0.02 | 9    | 0.224        | 4.77         | 95.50| 382.02| 2.582  | -15.721     | 0.02       | 0.053      | 4.94  | 6      | 98.93        | 395.75     | 0.053      |
| 1   | 0.02 | 0.02 | 8    | 0.209        | 4.79         | 95.81| 383.27| 2.583  | -16.225     | 0.02       | 0.037      | 4.96  | 2      | 99.25        | 397.00     | 0.037      |


From the observation of Table (4) and Figures (5) and (6), we find that the highest adsorption percentage for Nano-iron oxide was (R%=99.251) at the temperature (328) kelvin, while the highest adsorption percentage for activated carbon was (R%=95.819) at the same temperature, and the lowest adsorption percentage for Nano-iron oxide was (R%=98.315) at temperature (298) kelvin, while the lowest adsorption percentage for active carbon was (R%=94.570) at the same temperature, and it was found that adsorption increasing with increasing temperature, This means adsorption is endothermic process and this is in agreement with [18].

4. Conclusion

Based on the research results the (Nano FeO / CA) can be used as an available, cheap and adsorbent material to efficiently remove Safranin dye from its aqueous solutions. The Nano FeO / CA given a better removal rate than CA. Related, the dye removal efficiency is affected by several factors (Temperature, time, pH, adsorption capacity). The study showed the effect of the pH in the dye adsorption process was at (pH = 1) and the effect of shaking time on the adsorption process at 10 min to dye removal. Although, the effect of temperature on the dye adsorption process endothermic process was positive at (ΔH), the (ΔG) was negative value indicated the interaction automaticity. The (ΔS) values indicated the stability of the adsorption process.

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