Thermodynamic and kinetic studies of Eriochrome black adsorption on activated charcoal prepared from lemon leaves

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Abstract
The research included the preparation of activated carbon with nanoscale from the fallen leaves of lemon trees. The activated carbon was characterized using the following techniques: FT-IR, XRD, AFM, EDX and SEM. The results showed that the activated charcoal does not contain any active group, (i.e. chemically inert), has nanoscale particle and excellent porosity. Some of its physical properties, such as humidity (8%), ash (0.1 g), density (0.4 g cm$^{-3}$) and pH (7.2) were studied. The results of the adsorption process showed that the appropriate concentration of the Eriochrom black was 30 mg l$^{-1}$ and the appropriate weight of the new activated carbon was 0.07 g under equilibrium time of 25 min. The adsorption process is subjected to the psedusecond-order equation according to the R$^2$ correlation coefficient of 0.9999. The thermodynamic functions of the adsorption process were calculated at different temperatures ($10^{\circ}$C–$50^{\circ}$C), where the adsorption process was found to be an exothermic process ($\Delta H = -$) thusly, the adsorption is physically occurred because it is less than 40 KJ/mole and the free energy is negative (G = -$). These thermodynamic results mean that the adsorption process occurs spontaneously with negative entropy value ($\Delta S = -$). Moreover, adsorption isotherms were calculated and the results showed that Freundlich and Langmuir were suitable to represent the adsorption process of the dye.

1. Introduction
The physical and chemical adsorption treatments using activated carbon have important applications in the purification of wastewater contaminated with azo dye (EBT) for its high efficiency when added to dilute solutions of various dyes. Due to the high cost of commercial carbon and the difficulty of obtaining it, there was an urgent need to find adsorbent surfaces derived from natural materials. Therefore, workers in this field are extensively interested in the search for good alternatives adsorbent with high efficiency depending on what is available in their areas. Due to the high cost of commercial carbon and the difficulty of obtaining it, there was an urgent need to find adsorbent surfaces derived from natural materials. Therefore, workers in this field are extensively interested in the search for good alternatives adsorbent with high efficiency depending on what is available in their areas. The agricultural wastes such as sawdust, peel of some fruits, palm fronds and tea leaves were extensively used for dye removal. Additionally, much fallen tree leaves have been used due to their no-cost and the most important point is to produce a clean environment [1, 2]. Lemon leaves are a potential new environmentally friendly waste for the preparation of activated carbon nanoparticles, as they are inexpensive, available and suitable for dye removal [3]. Several previous studies have been made in this topic where Yeung et al [4] prepared activated charcoal from coffee residues by chemical activation at a temperature of 600 $^{\circ}$C and the resulted AC has a large surface area which then characterized with SEM and FT-IR. In 2005, Ramadan et al [5] has been prepared activated carbon from coccus spp. by chemical activation, using fixed percentages of NaOH with varying proportions of cocus wood. Moreover, Z. Wang and L. Chen have been used ginko leaves for the
preparation of its related activated carbon. The resulting activated carbon was used for the adsorption process of dibutyl phthalate [6]. Additionally, Z. Wang et al have been used new and treated waste granular-activated carbon to study the kinetic and thermodynamic of Ni adsorption [7]. Another advanced study included preparation of activated carbon composite containing manganese oxide for removing CH2O from water [8].

2. Experimental part

2.1. Instrumentations

The electronic spectra were measured using UV–vis spectrophotometer (1650PC–SHIMADZU). The FTIR spectra were recorded using Spectrophotometer FT-IR (1S-IR Affinity—SHIMADZU). The XRD pattern of the prepared activated carbon was conducted using XRD Diffractometer model (XRD-6000, Shimadzu x-ray Diffractometer) in the range of 2θ = 0–80 degree. The AFM image was pictured using Atomic force microscopy-SPM AA3000. SEM and EDX measurements were conducted using Scanning electron microscopy-AIS2300C. Shaking water path type YCW012S was also used to shake the samples under different times.

2.2. Chemicals

In this study, fallen lemon leaves were collected from Alabayche city, Bghadad, Iraq. Sodium hydroxide and hydrochloric acid were purchased from Sigma-Aldrich. Eriochrome black dye was supplied from Fluka company. All other solvents and chemicals were purchased from Alfa-Aesar.

2.3. Preparation of activated charcoal from powdered lemon leaves

The activated charcoal was prepared from lemon leaf powder in two stages: the coking stage at 400 °C for two hours, and the activation phase by adding 12 g of NaOH solution to the carbonized powder of lemon leaves. Thereafter, the homogeneous mixture was put into the iron-enclosed ends capsule and heated for 2 h at 800 °C. Then the resulting activated charcoal was left to cool to room temperature and washed with deionized water several times. The mixture was neutralized with (0.1N, 0.4 ml) of hydrochloric acid to obtain neutral activated charcoal. Then the mixture was filtered and dried for 3 h at 50 °C [9, 10].

2.4. Spectral study

The maximum wavelength (a max) was determined by preparing a solution of the eriochrom black T for a spectral follow-up to take advantage of the ability of this dye to show a clear absorption band in the visible-ultraviolet region and the colour of blackish-purple which was 530 nm. The calibration curve was constructed at a range of concentrations 10–60 ppm using a spectral method to give a linear relationship, confirming that it is subject to Lambert-Bert low [11]. In addition to studying the optimal conditions for the dye removal and adsorption kinetics.

3. Results and discussion

It is known that the permissible range of moisture content of activated charcoal must be less than 9% [12]. In this work, the moisture content of the prepared activated charcoal was calculated to be 8% only, indicating our successful preparation method. Furthermore, the ash content of 0.1 g was 5%. This percentage is considered to be one of the allowable percentages in the international and commercial activated charcoal specifications which are in the range of 1%–5% of the total activated carbon weight [13]. Besides, the density of the prepared activated charcoal was demonstrated and the results show that our activated carbon has a high density of 0.4 g cm⁻³. This indicates that the prepared activated carbon has high adsorption efficiency compared to the previously prepared species [14]. The pH was measured by pH meter for activated carbon filtrate and found to 7.2, indicating that the prepared activated carbon is neutral and it is a good characteristic of common activated carbon.

3.1. Characterization of the prepared activated carbon

Activated carbon was characterized using the following techniques:

3.1.1. AFM

The main advantage of this technique is its ability to record the nanoscale size of the samples accurately and provide an accurate description of the size distribution without any mathematical processing [15]. The atomic force microscope result of the prepared activated carbon shows that the maximum height was 42.50 nm with a particle size distribution of 65–125 nm, as shown in figure 1.
3.1.2. FTIR
The FTIR spectrum of the prepared activated carbon was showed no-peaks, therefore, it is not containing any functional group effective group, indicating complete calcination and it is chemically inert as in figure 2.

3.1.3. XRD
X-ray diffraction for the powder was used to determine the crystalline form of the prepared nanoparticles by Miller indices \([16–20]\).

The purity of the prepared activated carbon (figure 3), as well as the calculation of the average size of the activated carbon nanoparticles, are determined using the Debye Scherer equation:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]  

Table 1 shows the XRD data obtained from the x-ray diffraction spectrum of the three sharpest peaks, which was used to calculate the average crystal size of the activated carbon sample which was found to be 18.35 nm, confirming that the prepared activated carbon contained nanoscale particles.
3.1.4. SEM and EDX

The SEM measurement showed that the activated carbon has an unlimited number of white nanoparticles within the range (300–800 nm) figure 4. These nanoparticles will give this material more ability to adsorption or retention of dye molecules within the sample of activated charcoal produced from lemon leaves. The size of the pores was calculated from figure 5 and was found to be within the range of 600 nm to 2 microns. Figure 6 also demonstrates the presence of small white particles scattered in pores. The presence of these small particles within the pores will certainly add another blocking factor and therefore the adsorption within our activated carbon will be very high.

The EDX analysis (figure 7) for this sample showed that there were seven elements involved in the composition of this sample. The measurement showed a carbon signal at 0.277 KeV (85.58%), while oxygen was 11.33% which gave a signal at 0.525 KeV. The measurement also showed the presence of calcium (2.00%) and potassium (0.13%) and magnesium (0.76%) while phosphorus (0.17%) and zinc at very low per cent which did not exceed 0.04% at K-alpha 3.690 KeV, 3.312 KeV, 2.307 KeV and 8.630 KV, respectively.

### Table 1. Data of the three sharpest peaks in the x-ray diffraction.

| No. | 2Theta (degree) | I/I1 | FWHM  |
|-----|----------------|------|-------|
| 1   | 31.6014        | 100  | 0.92  |
| 2   | 37.1893        | 93   | 0.41  |
| 3   | 36.0470        | 79   | 0.30  |

3.2. Spectroscopic method of adsorption

Using the spectroscopic method of adsorption, the results gave a linear relationship which confirms that they are subject to Lambert–Beer’s law, which gives the plot between the absorption values with the concentrations as shown in figures 8 and 9 where the amounts of residue and adsorbed were determined in the solution.
The results showed that the adsorption process reached the equilibrium state during a period of time ranging between 25–30 min as in table 2 which gave the highest adsorption efficiency. In the case of equilibrium, we note that the increase in the equilibrium time did not enhance the adsorption process of the dye due to the lack of vacant sites (pores) of adsorption, which leads to return to the solution \([21]\) because of the extortion process. The effect of primary concentration and adsorbent weight was also studied and illustrated in tables 3 and 4, respectively.

The appropriate concentration was 30 ppm which was chosen to give the highest adsorption efficiency and that 0.05 g of AC represents the optimal adsorbent weight which gave a capacity capable of absorbing the largest amount of EBT dye. One of the kinetic model (second-order false model) was applied to the practical results of the studied adsorption system as in the following equation \((1)\).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e}$$

(2)

The value of the practical adsorption capacity \((q_e)\) is correlated to the theoretically calculated value \((q_e)\) and that the good R-value indicates that the adsorption system follows the equation of the second-order \([22]\) as shown in figure 10 and table 5.

The effect of temperature on the equilibrium constant was studied and the results proves that the adsorption efficiency decreases with increasing temperature \([23, 24]\) as shown in table 6.

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

(3)
Note that the negative value of $(\Delta H)$ indicates that the process of adsorption of EBT dye on the surface of activated carbon is exothermic process as shown in figure 11. Furthermore, the results show that the adsorption is physically occurred because the forces responsible for the process of adsorption are weak. The results also show that the adsorption process occurs spontaneously by calculating the values of change in free energy $(\Delta G)$ and note that negative $\Delta S^0$ values reduce the randomness of the studied system, for the loss of molecules after adsorption, and this is consistent with the previous study [25].

Two models of adsorption isotherms were used; Freundlich [26] (figure 12) and Langmuir [27] (figure 13), which were calculated from the following equations table 7:
It can be easily seen from the values of the Freundlich and Langmuir constants that the Langmuir model is more appropriate than the Freundlich model by comparing the results obtained as shown in tables 8 and 9.

Table 2. Determination of equilibrium time and adsorption efficiency.

| Time (min) | Absorption (mg/L) | C_e (mg/L) | Adsorption (%) |
|------------|-------------------|------------|----------------|
|            |                   |            |                |
| 0          | 0.394             | —          | —              |
| 5          | 0.171             | 5.634      | 24.366         | 81.22 |
| 10         | 0.151             | 3.483      | 26.517         | 88.39 |
| 15         | 0.148             | 3.161      | 26.839         | 89.46 |
| 20         | 0.146             | 2.946      | 27.054         | 90.18 |
| 25         | 0.145             | 2.838      | 27.162         | 90.54 |
| 30         | 0.145             | 2.838      | 27.162         | 90.54 |
| 35         | 0.147             | 3.053      | 26.947         | 89.82 |
| 40         | 0.149             | 3.268      | 26.732         | 89.10 |
| 45         | 0.151             | 3.483      | 26.517         | 88.39 |
| 50         | 0.148             | 3.161      | 26.839         | 89.46 |
| 55         | 0.152             | 3.591      | 26.409         | 88.03 |
| 60         | 0.150             | 3.376      | 26.624         | 88.74 |

\[ Q_e = k f (C_e)^{1/n} \]  \hspace{2cm} (5)

\[ Q_e = a C_e / (1 + b C_e) \]  \hspace{2cm} (6)

It can be easily seen from the values of the Freundlich and Langmuir constants that the Langmuir model is more appropriate than the Freundlich model by comparing the results obtained as shown in tables 8 and 9.
4. Conclusion

In this work, we demonstrated the possibility of using lemon leaf residues as a source for the preparation of activated charcoal with micropore humidity (8%), ash (0.1 g), density (0.4 g cm$^{-3}$) and pH (7.2). Furthermore, our study involved thermodynamic calculations of the Langmuir and Freundlich relationships and compared the results with each other and found that the substance was able to remove more than 91% using 0.07 g at the optimum temperature of 25°C for 25 min. The adsorption process is subjected to the pseudosecond-order equation according to the R$^2$ correlation coefficient of 0.9999. The following botanical sources; rice husk [28],

![Figure 10. The application of the pseudosecond-order equation on the adsorption system of EBT dye](image)
Figure 11. EBT adsorption on the surface of activated carbon using the Van’t-Hoff equation.

Figure 12. Freundlich isotherm of the adsorption system.

Figure 13. Langmuir isotherm for adsorption system.

Table 7. Thermodynamic values for EBT adsorption on activated carbon at different temperatures.

| T(K)  | ΔH° (J.mole⁻¹) | ΔG° (J.mole⁻¹) | ΔS° (J.mole⁻¹.K⁻¹) |
|-------|----------------|----------------|---------------------|
| 283.15| 40620.54       | -6849.18       | -119.33             |
| 293.15| -6185.00       | -117.52        |                     |
| 298.15| 5594.35        | -117.53        |                     |
| 303.15| -4060.85       | -120.65        |                     |
| 313.15| -4137.62       | -116.55        |                     |
| 323.15| -1928.13       | -119.7         |                     |
Table 8. Values of lnCe and lnQe for the adsorption at different concentrations according to Freundlich equation.

| C0 (M) (mg/L) | lnCe | lnQe | k (mg/g) | N (L/mg) | R² |
|---------------|------|------|---------|----------|----|
| 20            | –3.146 | 3.686 | 55.75   | 9.208    | 0.9067 |
| 30            | 1.043  | 3.994 |         |          |    |
| 40            | 2.118  | 4.148 |         |          |    |
| 50            | 2.585  | 4.296 |         |          |    |
| 60            | 2.931  | 4.412 |         |          |    |

Table 9. Ce and Ce/Qe adsorption values at different concentrations according to the Langmuir equation.

| C0 (ppm) | C0 (mg/L) | Ce/Qe (g/L) | a (mg/g) | b (b/L/mg) | R² |
|----------|-----------|-------------|----------|------------|----|
| 20       | 0.04302   | 0.00        | 68       | 0.816      | 0.9798 |
| 30       | 2.837     | 0.0522      |          |            |    |
| 40       | 8.314     | 0.131       |          |            |    |
| 50       | 13.203    | 0.18        |          |            |    |
| 60       | 18.746    | 0.227       |          |            |    |

tridax procumbens [29] and monotheca buxifolia seed [30] were used to prepare their related activated carbon for the studies of removing the EBT from water samples. These materials gave a dye removal of 99.83, 78 and 82.5%, while activated charcoal prepared by us had a maximum removal value of 94.84%.

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