Study Of Effect Adsorption Of E127 Dye By Iraqi Clay From Aqueous Solution

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Abstract

The surface of kaolin was diagnosed by an AFM and the results were shown The height of the highest peak reached by a quantity of Kaolin surface is 2.5 µm, the granules, and their diameter with an average diameter of 666.1nm. Using Kaolin's adsorption properties, erythrosine was removed of its aqueous solution. It was determined that the maximal dye adsorption ranged 36.53–40.61%. The results of using the Freundlich, Langmuir, and Temkin adsorption isotherms revealed that at temperatures of (298,308,318) K, The Langmuir model did not fit, and the Temkin model could only be used partially, and the Freundlich model was used Because it is the most applicable of the three models. There is also physical adsorption. One of the three kinetic models of the adsorption process that was examined, the pseudo-second-order model, was found to be applicable significantly based on the result. Using the enthalpy value to calculate the thermodynamic functions, the process was proven to be exothermic, which was negative and equal to (-16.5582kJ/mol). The entropy value, which equaled (-2.2696J*mole⁻¹*K⁻¹), was also negative. Calculating the Gibbs free energy, it was discovered that the process is exothermic adsorption, non-spontaneous, and happens without randomization.

Keywords: Kaolin; Pollution; commercial food dye; Atomic force microscope.
Pollution is defined as any substance that is added to the environment, whether it is in a liquid, solid or gaseous state. Pollution is one of the biggest problems facing humans and the environment in particular [1], because of its importance in all areas of life. This pollution often occurs because of throwing organic waste, petrochemical waste, petroleum and industrial materials, and other waste [2].

Water tainted with organic dyes is one of the dangers to human life. Industrial dyes are thought to be water contaminants that might be dangerous. Environmental contamination is still a problem, and when the poisons exhibit persistence and refractory nature, the situation only grows worse. This group includes artificial colors of the xanthene family in particular [3].

Due to their ability to adsorb significant quantities of contaminants in soil, clay plays a significant part in pollution issues. Toxic heavy metals like mercury, cadmium, and lead may readily exchange with cations of harmless elements like sodium and calcium that are typically associated to clay particles in organic pollution. Due to its enormous surface area and ability to engage in a variety of molecular interactions other than ion exchange, clay may bind a huge number of organic contaminants [4].

A soft, white mineral with many applications is kaolin. Kaolin is widely available in Nigeria, where it is mostly used to make porcelain. It has been researched and shown to be successful in removing hazardous metals from waste water. It was discovered to be efficient in the adsorption of Congo Red, hexavalent chromium, nitrate, and methylene blue from aqueous solution [5].

The food colour erythrosine (E127), a synthetic color belonging to the xanthene family[6]. Erythrosine is a common color used in a variety of sectors, including cosmetics, pharmaceuticals, and the food industry, notably for biscuits, chocolate, luncheon meat, sweets, and chewing gum. [7]. Erythrosine is highly soluble in water (70g/L) and has good stability in neutral and basic solutions. The chemical structure of the synthetic erythrosine is shown in Fig. 1. [8].

Figure 1. Chemical structure of Erythrosine [8].
2. Materials and method

2.1 Preparation of Erythrosine stock solution

The erythrosine dye, one gram, was dissolved in de-ionized distilled water in a beaker to create the standard solution, which was then diluted in a (1000 ml) volumetric flask. The dye solution was made in a range of concentrations ranging from 4.0 to 60.0 mg/L.

2.2 Preparation of Kaolin

In order to wash the Kaolin clay, a sufficient amount was taken and put in a glass beaker. The clay was then washed for 10–12 times with de-ionized distilled water to remove any contaminants suspended on the surface. The surface was dried for six hours at 100 °C in a lab oven. An electric grinder was used to grind the dry surface. The Kaolin was sieved through a molecular sieve with a granular size (75µm). Then, it was stored in a plastic container for the investigation.

2.3 Kaolin surface diagnostics by atomic force microscopy (AFM)

Atomic force microscope is a high-resolution microscope with a very high analysis capacity, when compared to optical microscopes, it exceeds them by 1000 times, as it reaches parts of nanometers in diagnosing samples and gives two- and three-dimensional images of the surface [9].

The AFM device was used to probe kaolin surface topography by taking two-and three-dimensional images, as shown in Fig2. The results of examining a sample crushed by a sieve with a granular size (≤75µm) showed the following:

The height of the highest peak reached by a quantity of Kaolin surface is 2.5 µm, as shown in Fig2

**Figure 2.** (a) 3D and (b) 2D image of the surface of kaolin under the AFM.

The particle analysis showed the data shown in Fig.3 and Scheme 1 to vary in the distribution of the granules, and their diameter ranged between 1699 nm and 61.01 nm, with an average diameter of 666.1 nm. According to the follow-up of the chart. It was found that, the largest number of granules is smaller than 400 nm, in addition to the presence of other granules with a larger diameter.
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<table>
<thead>
<tr>
<th>Parameters</th>
<th>Projected Area</th>
<th>Projected area</th>
<th>Mean diameter</th>
<th>Z max...</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle #1 Small</td>
<td>9477</td>
<td>61.01</td>
<td>1210</td>
<td></td>
</tr>
<tr>
<td>Particle #2 Large</td>
<td>36099</td>
<td>181.1</td>
<td>1259</td>
<td></td>
</tr>
<tr>
<td>Particle #3 Large</td>
<td>290312</td>
<td>547.5</td>
<td>2513</td>
<td></td>
</tr>
<tr>
<td>Particle #4 Large</td>
<td>405717</td>
<td>621.1</td>
<td>2578</td>
<td></td>
</tr>
<tr>
<td>Particle #5 Large</td>
<td>230278</td>
<td>1699</td>
<td>1577</td>
<td></td>
</tr>
<tr>
<td>Particle #6 Large</td>
<td>169269</td>
<td>391.3</td>
<td>2578</td>
<td></td>
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<tr>
<td>Particle #7 Large</td>
<td>749413</td>
<td>888.1</td>
<td>2286</td>
<td></td>
</tr>
<tr>
<td>Particle #8 Small</td>
<td>15475</td>
<td>96.49</td>
<td>1214</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.** Analysis data of kaolin surface particles under an atomic force microscope

**Scheme1.** The granular distribution of the surface of kaolin according to the diameter of the granules.

2.4. Determination of $\lambda_{\text{max}}$ for Erythrosine dye

Using a standard solution of E127, its maximum wavelength ($\lambda_{\text{max}}$) was determined. It was being measured between (190-800 nm) in a visible and ultraviolet spectrophotometer. The E127's maximum wavelength of absorption is (526nm). A quartz cell with a 1 cm thickness was used for the measurement.

**Figure 4.** UV-visible absorption spectrum of E127.

The absorption spectra of the E127 dye is shown in Fig 4. .
3. Results and Discussion

3.1. Effect of the adsorbent weight (Kaolin) on the adsorption ability

In order to investigate the ideal weight for the used kaolin to remove E127 dye by adsorption on the surface of the Kaolin, the impact of Kaolin's weight was examined utilizing a primary dye concentration 60mg/L opposed to a sequence of different weights of the Kaolin 0.05 to 0.7g at 298K. According to the results shown in Fig. 5, it was found that as the amount of active sites produced for E127 adsorption was increased, the effectiveness of the adsorbent surfaces improved in their capacity to take the dye out of its water-based solution. The weight of the Kaolin rose by 0.05 to 0.10 g, which was equal to 36.53 to 40.61%, increasing the percentage of removal %R constantly. At the optimum weight of 0.2 g. of the Kaolin, which was equivalent to 45.32%, the percentage of elimination then turned to remain constant due to saturation of all adsorption sites at the kaolin surface [10].

Figure 5. Effect weight of the Kaolin on adsorption of E127 dye.

3.2. Investigation of the equilibrium time

At various temperatures (298,308, and 313) K and starting dye concentrations of 60 mg/L , the effects of the equilibrium time of Kaolin with the aqueous solution of E127 dye have been studied, granule size (≤75µm), and the ideal weight of Kaolin 0.2g. Fig.6 depicts how the adsorption process of the adsorbent surface Kaolin is
Figure 6. Effect of equilibrium time on the amount of E127 dye that was adsorbed on the surface of Kaolin.

affected by time. The outcomes show that equilibrium period for the E127 dye desorption process on Kaolin is 30 minutes.

3.3. Adsorption Kinetics Models studies

The adsorptive behavior of erythrosine (E127) on Kaolin was investigated using the pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich kinetic models. The following is the stated linear form of PFO. [11].

\[
\ln(q_e - q_t) = -K_1 t + \ln q_e \quad 1
\]

qt(mg/g) stands for the capacity for adsorption at time, qe(mg/g) for the capacity for adsorption at equilibrium, and K1 for the rate constant for adsorption min\(^{-1}\). K1 is calculated using the slope of the in (qe-qt) vs. time (t) linear plot, as illustrated in Fig.7a.

The formula (2) is used to determine Pseudo first order constants [12].

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad 2
\]

K2(g mg\(^{-1}\). min \(^{-1}\)) is the adsorption rate constant for the (PSO) process. According to Fig. 7b, K2 is computed from the intercept of the linear plot of t/qt vs. time(t).

Constants determined \(\alpha\), \(\beta\) by the formula (3) is used to determine (Elovich) constants [13].

\[
q_t = \frac{1}{\beta} \ln(\beta \alpha) + \frac{1}{\beta} \ln t \quad 3
\]

\(\alpha\) stands for the desorption process constant in (mg.g\(^{-1}\).tim\(^{-1}\)) units, while \(\beta\) stands for the initial adsorption rate constant in units (g.mg\(^{-1}\)). Moreover, both and are calculated from the slope and intercept in Fig.7c.
Due to the strong ($R^2$) values and convergence of the theoretical and actual values of ($q_e$), as shown by Table 1's findings and a study of the $R^2$ values for each of the three Kinetic models, the PSO and Elovich are applicable. The PFO Kinetic models could not be employed since there were relatively few ($R^2$) values and the real ($q_e$) values did not resemble the theoretical values [15,16].

Figure 7. The PFO (a), PSO (b), Elovich (c) kinetic models for the E127 dye's adsorption on the Kaolin surface at various temperatures.

Table 1 The values of the kinetic constants of the adsorbent Kaolin surface at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Elovich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>298</td>
<td>-0.1319</td>
<td>0.0176</td>
<td>0.4509</td>
</tr>
<tr>
<td>308</td>
<td>-0.0813</td>
<td>0.0306</td>
<td>0.3718</td>
</tr>
<tr>
<td>318</td>
<td>-0.0664</td>
<td>0.0513</td>
<td>0.3052</td>
</tr>
</tbody>
</table>

3.4. Adsorption isotherms

An array of different concentrations of E127 10-45mg/L and temperatures (298,308,and318)K were used, together with the ideal adsorbent surface weight of Kaolin (0.20g.), particle size (75 µm), equilibrium period (30 min), to examine the adsorption isotherms. Fig. 8 illustrates the link between the ($q_t$(mg/g) and ($C_e$ (mg/L)) isotherms of the E127 dye's adsorption on Kaolin at different temperatures.

Figure 8 Isotherm for adsorption of E127 dye over Kaolin

According to Freundlich's adsorption principles, Figure 6 illustrates the dye adsorption isotherm on surface E127 of type (S2). This demonstrates that different forces are used throughout the adsorption process on the adsorbent surface, according to Giles' classification. The amount of adsorbate material on the surface reduces as
the covered area of the adsorbent surface increases\[17\]. The adsorbate will occupy a smaller portion of the adsorbent surface areas because the adsorption process occurs perpendicular to the adsorbent surface. As a result, there will be a high amount of adsorption and unoccupied areas on the surface with the potential for adsorption be high\[18\].

3.5. Adsorption Isotherm Models.

Table 2 provides results for the Freundlich, Langmuir, and Temkin model constants as well as correlation coefficients after three models of the adsorption process isotherm were applied to the acquired data. The isotherm models for the adsorption process are shown in Fig.9. The Freundlich model constants (Kf (mg/g)) and (n) were derived using equation (5)\[19\].

\[
\log(q_e) = \log(K_f) + \left(\frac{1}{n}\right) \log(C_e) \quad (5)
\]

The Langmuir constants K_L (L/mg) and qe_max (mg/g) were derived using formula (6)\[20\].

\[
\frac{C_e}{q_e} = \frac{C_e}{q_e max} + \frac{1}{q_e max K_L} \quad (6)
\]

Temkin constants (L/mg) and B_T (J/mol) were accounted for using formula (7)\[21\].

\[
q_e = B_T \ln K_T + B_T \ln C_e \quad (7)
\]

Figure 9 Figure 9. Langmuir (a), Freundlich (b), Temkin (c) isotherms for adsorption of E127 dye over Kaolin surface at different temperatures.

Table (2) The values of the isotherm constants of the adsorbent surface Kaolin at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_f (mg/g)</td>
<td>n</td>
<td>R²</td>
</tr>
<tr>
<td>298</td>
<td>0.2037</td>
<td>1.2132</td>
<td>0.8986</td>
</tr>
<tr>
<td>308</td>
<td>0.1615</td>
<td>1.1169</td>
<td>0.9668</td>
</tr>
</tbody>
</table>
Table 2, shows that values of (n) are restricted to being between (1-10) and that Freundlich's isotherm equation is quite applicable to the adsorption process in this experiment. This shows that adsorption is governed by physical forces. Moreover, the exothermic character of the adsorption process is supported by the fact that the Freundlich constant (K_f) for the adsorbent surface Kaolin decreases as the temperature under observation rises. And the adsorption process took place on surfaces that were heterogeneous and had a variety of adsorption energy sites [22]. Because of the comparatively low linear correlation coefficient at the same test temperatures, the findings in Table 2 demonstrate that the Langmuir model does not fit[23]. Given that the surface correlation coefficient is less than 0.9 at all temperatures, Temkin's model is likewise only partially applicable[24].

3.6. Thermodynamic study for adsorption of E127 over kaolin

To demonstrate the effect of temperature on the behavior of the adsorption process, thermodynamic constants such as Gibbs free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) were calculated [25]. The values of the thermodynamic functions are shown in Table 4. for the adsorption of an E127 dye on adsorbent surface Equation (8) was used to compute the equilibrium constant for E127 dye adsorption process on the Kaolin in order to estimate the values of the thermodynamic functions at each temperature[26].

![Figure 10. Vant Hof's equation for adsorption of E127 dye on the adsorbent surfaces of Kaolin.](image)

\[ K_{eq} = \frac{q_{eq} \times w(g)}{C_e \times V(L)} \]  \hspace{1cm} (8)

In order to calculate ΔH° and ΔS°, plot Fig. 10 between lnKeq and 1/T from table 3, where the intercept is denoted by S°/R and the slope by (- ΔH°/R). [27].

\[ \ln K_{eq} = \frac{-\Delta H^°}{RT} + \frac{\Delta S^°}{R} \]  \hspace{1cm} (9)
Table (3) Thermodynamic values of the adsorption of E127 dye on the adsorbent surface of the Kaolin at different temperatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T</th>
<th>1/T (K⁻¹)</th>
<th>Kₑq</th>
<th>Ln Kₑq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>298</td>
<td>0.0034</td>
<td>0.341</td>
<td>-1.0759</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>0.0032</td>
<td>0.3314</td>
<td>-1.1044</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.0031</td>
<td>0.3219</td>
<td>-1.1335</td>
</tr>
</tbody>
</table>

Equation (10)[28] is used to compute the change in the Gibbs free energy.

\[ \Delta G° = -RT\ln Kₑq \quad \text{(10)} \]

Table (4) values of the thermodynamic equilibrium constants for adsorption of E127 dye on the adsorbent surface of Kaolin and at different temperatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T (K)</th>
<th>( \Delta G° ) KJ/mole</th>
<th>( \Delta H° ) KJ/mole</th>
<th>( \Delta S° ) J/mole.k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>298</td>
<td>2.6656</td>
<td>-16.5582</td>
<td>-2.2696</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>2.8281</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>2.9968</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The enthalpy of the adsorption process on the Kaolin demonstrates the exothermic nature of the adsorption process, and the enthalpy values were less than (40 KJ/mol), verifying physical adsorption [29]. The negative entropy values make it clear that the dye adsorption process on the surface is regular and not random. For the E127 dye adsorption on Kaolin, positive Gibbs free energy values demonstrate that the adsorption process is not spontaneous[30].

Conclusions

In this experiment, erythrosine dye was adsorbed by bentonite with a removal rate of 45.32%. The (PSO) model has the best match, according to the findings of the used kinetic constants. being compatible with the Freundlich isotherm in addition. The negative values of \( \Delta G° \) indicate that the adsorption process is not spontaneous, in addition to the negative value of \( \Delta S° \) and \( \Delta H° \), which indicates that the adsorption process is increasing in regularity, and it is an exothermic and physical process.

References


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