

GRAPHENE CALCIUM FERRITE NANOCOMPOSITE EFFECTIVELY ADSORBS AND REMOVES THE TOXIC ACID BLUE 25 DYE FROM AQUEOUS MEDIUM

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Abstract: The modified Hummers technique was employed in this study to make a graphene CaFe₂O₄ composite that was used as an adsorbent to remove acid blue 25 dye from aqueous solution. XRD, SEM and TEM were employed to characterize the adsorbent. Acid Blue 25 was adsorbed using the resulting adsorbent under a variety of experimental settings. Within 240 minutes, the initial fast adsorption of dye species achieved equilibrium. With a rate constant of $8.49 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ at 303 K, the interactions were much closer to second-order kinetics. 100.0 mg g⁻¹ was the Langmuir monolayer capacity at 303 K. The interaction was endothermic with ΔH 60.7 KJ mol⁻¹ accompanied by a rise in entropy and a decrease in Gibb's free energy.

Keywords: Adsorption, Isotherm, Acid blue, Nanocomposite.

1. Introduction:

The outflow of untreated or poorly treated effluents from many companies has caused aquatic streams' water quality to decline, raising concerns across the globe [1]. One of the primary draws of textiles and other items made from the textile industry is color. Nonetheless, the main contaminant in the textile wastewater generated during its production chain is the dye used for the colorization process [2]. The three main types of dyes used in industrial applications are cationic, anionic, and non-ionic [3], and the dyes that contain functional groups in their chemical structures are azo, anthraquinone, phthalocyanine, indigo, nitro, and sulfur [4]. The problem of artificial dye pollution has gained worldwide interest due to the fact that even trace amounts of these dyes are visible in water, have the potential to cause cancer in humans, and adversely affect the natural marine environment [5]. The presence of coloring chemicals on surface bodies harms the aquatic biota since they obscure sunlight, which limits photosynthesis and limits the level of dissolved oxygen in the water [6]. The dye's ability to mix with another synthetic substance or degradation product might create another issue, leading to substances causing cancer [7]. The acid blue 25 (AB 25) dye, an anionic molecule that has an anthraquinonic structure, is the subject of this study [8]. This dye can be taken in by mouth, inhalation, or absorption through the skin [9, 10]. Coughing and inflammation of mucosal membranes and the upper respiratory tract may arise from inhalation exposure [11]. Furthermore, it may cause severe skin or eye irritation, redness, itching, and/or allergic skin reactions on contact [12]. It can irritate the mucosa of the stomach and digestive tract, cause diarrhea, and harm essential bodily organs when inhaled [13]. Adsorption technology draws a lot of research attention among the various possible treatments because of its advantages in terms of efficacy, economy, and efficiency [14]. Adsorption involves a surface phenomenon that arises from interactions among individual atoms, molecules or ions of an adsorbate adsorbent system. A variety of methods were introduced in adsorption process, which can change how pollutants are distributed through the subsurface system's constituent phases and interfaces and explain how a substance isolates from one phase and deposits at the surface of another [15,16]. A lot of adsorbents are used to remove various contaminants from aqueous solution. This includes zeolites [20], clay and clay minerals [18,19], inorganic oxides [17], and other materials. All of these adsorbents do, however, have limitations, either in terms of their adsorption capabilities or in terms of the difficulty of separating the materials once they have been loaded with pollutants. In recent years, one kind of carbon, namely graphene and its derivatives has attracted a lot of interest as an adsorbent for purifying wastewater.

Graphene (GN) is a 2D dimensional six-member honeycomb lattice. Long-range π -conjugation in graphene provides remarkable and distinctive features, although its theoretical surface area ($2,630 \text{ m}^2 \text{ g}^{-1}$) is more significant in this case [21]. Graphene (GN) is a perfect building block for nanocomposites owing to all of these characteristics. The large surface area increases the interfacial interaction with other materials. Additionally, GN's vast surface area keeps secondary components from aggregating, sustaining some of its special nanoscale characteristics [22]. Pollutant removal has been studied using graphene and its metal oxide composites as adsorbents [23,24]. Graphene oxide (GO), a derivative of graphene, has attracted a lot of attention from researchers in addition to graphene because of its well-organized sp^2 -hybridized carbon nanostructures and extensively distributed, higher specific charged surface area [25,26]. GO is also prepared from natural graphite using a chemical oxidation-exfoliation-reduction process [27]. Numerous functional groups containing oxygen are linked to the GO during the chemical oxidation process [28,29]. This substrate's altered surface structure makes it perfect for anchoring a large number of inorganic nanoparticles and encouraging wider use [30,31]. It is reported that calcium ferrite, a magnetic Ca-Fe oxide material with Ca^{2+} and Fe^{3+} ions in the spinel structure, has important features useful in various applications [32]. However, graphene-based nanoparticles have allegedly only been tested in a few number of studies as an adsorbent for eliminating contaminants. A significant number of published publications that included the synthesis and application of different GO-based nanostructures for extraction from the aqueous environment were evaluated by Lu et al. [33]. Wang et al. [34] utilized Fe_3O_4 -GO nanocomposite to remove fuchsin from aqueous solution. Furthermore, the GO/ZnO composite has been reported to be employed as a reusable adsorbent for managing pollutants [35]. Xie et al. [36] described the synthesis and adsorptive use of a super-paramagnetic GO- Fe_3O_4 hybrid composite. Taking these advantages, in the present work, the magnetic spinel calcium ferrite-graphene composites have been tried as adsorbents for the removal of organic dye acid blue 25 (AB 25), which has not been reported earlier. The present investigation focuses on removing AB 25 from aqueous solution with Graphene Calcium Ferrite nano (GCF) composites as a magnetic adsorbent.

2. Experimental:

2.1. Materials and methods:

The Graphene powder purchase from Swiss company SIGMA-ALDRICH CHEMIE, GmbH. All other chemicals and reagents, including $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, H_2SO_4 (98%), KMnO_4 , and H_2O_2 (30%), were received from E-Merk, Mumbai, India. The Indians India's SDFine Chemical Ltd. Mumbai provided H_3PO_4 (85%).

Mark Chemical Laboratory Reagent Co. Ltd., (Worli, Mumbai) also provided the AB 25 (Molecular formula: $\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}_5\text{S}$, CI Classification number: 62055). All of the chemicals were of analytical quality and got used without further purification.

2.2. Preparation of Graphene oxide:

Graphite flakes (1.5 g) and KMnO_4 (9.0 g) were slowly added to a 9:1 ratio of concentrated H_2SO_4 and H_3PO_4 acids while being continuously stirred in order to form GO using the modified Hummer's methods [37, 38]. The reaction mixture was heated to 323 K for 12 hours with constant stirring. Then cooling and added to 30% H_2O_2 in ice. The mixture was dried at 353 K after being repeatedly cleaned with ethanol and 30% HCl.

2.3. Preparation of graphene-calcium ferrite composite:

After sonicating 1.0 g of graphene oxide (GO) for one hour, 0.118 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.404 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were then added while stirring continuously. After being sterilized by autoclave for four hours at 393 K, the mixture was allowed to return to room temperature before being washed with water and oven-dried.

2.4. Batch adsorption study of dye:

In a batch process, dye in aqueous solution was adsorbed on the formed CFO-GOC. Typically, a thermostated water bath shaker (Superior Scientific Industries, Timber Market, Ambala, Haryana, India, ISO 9001:2008) was used to shake 50 mL of dye solution with the desired initial concentration after the adsorbent of the desired quantity was introduced. At the pre-determined time interval, the solution separated from the mixture by centrifugation. The concentration of dye in the supernatant solutions was measured by a visible spectrometer (Elico Limited SL 177, Hyderabad, Andhra Pradesh). Dropwise additions of 0.01 N NaOH and 0.01 N HNO₃ solutions were employed to maintain the pH of the adsorbate solution. The changes between the aqueous solution concentrations before and after adsorption were used to determine the adsorbed amount and the percentage of dye removal using the relations

$$q_e = (C_0 - C_e) V/m \quad (1)$$

$$\text{Extent of adsorption (\%)} = (C_0 - C_e / C_0) \times 100 \quad (2)$$

In this context, q_e represents the quantity of adsorbate adsorbed (mgg⁻¹) per gram of the adsorbent at equilibrium C_0 (mg L⁻¹) and C_e (mg L⁻¹) represent the initial and equilibrium concentrations of the dye, respectively.

V (L) represent the volume of the solution taken, and m (g) represent the mass of the adsorbent.

The adsorption process was investigated under different experimental conditions including the effect of solution pH of the solution, initial dye concentration, adsorbent load and contact time. The different experimental conditions are listed in table 1.

Table 1: Experimental conditions for adsorption study

SI No.	Parameter for adsorption process	Experimental set-up conditions
1	Influence of pH of the solution	Adsorbent 0.1 g L ⁻¹ , temperature 303 K, time 240 min, pH 2.0–11.0, dye concentration 10 mg L ⁻¹
2	Influence of dye concentration	Adsorbent 0.1 g L ⁻¹ , pH 6.8, time 240 min, temperature 303 K, dye concentration 10–30 mg L ⁻¹
3	Influence of adsorbent dose	Dye concentration 10 mg L ⁻¹ , pH 6.8, temperature 303 K, time 240 min, adsorbent dose 0.02–0.18 g L ⁻¹
4	Influence of interaction time	Adsorbent 0.1 g L ⁻¹ , pH 6.8, temperature 303 K, dye concentration 10 mg L ⁻¹ , time 10–240 min

Characterization:

A Bruker AXS (Germany) diffractometer, Model D8, was utilized for the XRD measurements. Cu K α monochromatized radiations with a step size of 0.02° (2 θ) were used. The topography of the surface was investigated utilizing a High Resolution Transmission Electron Microscopy (HRTEM) with a JEM-2100, Jeol, Akishima, Japan. The morphological structure was acquired utilizing the Zeiss FESEM (model Sigma) for the Field Emission Scanning Electron Microscopy (FESEM) images.

3. Result and discussions:

3.1. XRD study:

The broad diffraction peaks in the X-ray diffractogram (Figure 1) indicated that the mean crystallite size was in the range of nanometers. The XRD spectra of the CaFe₂O₄-GO composite demonstrated an absence of distinct

diffraction peaks for GO (0 0 1). The reduction of graphene oxide to graphene in the hydrothermal process in the presence of alcohols may account for an absence of the GO (0 0 1) signal.

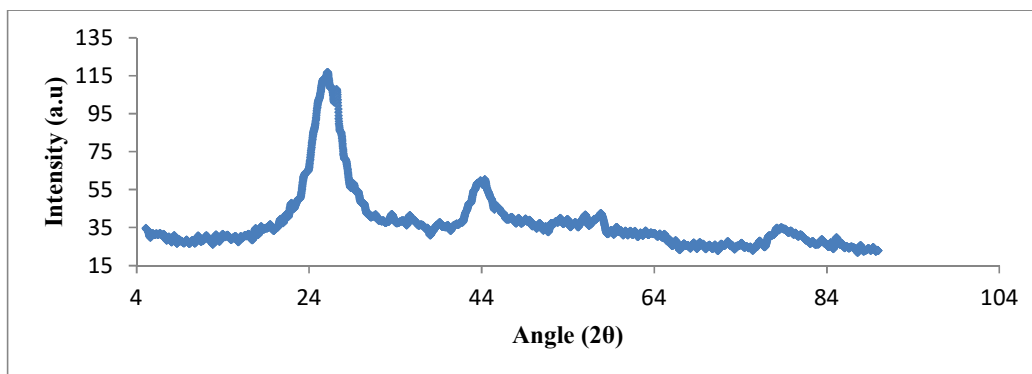


Figure1: XRD of CaFe_2O_4 -GO composite

3.2 TEM Analysis:

The HRTEM measurement may verify the synthesis of the CaFe_2O_4 -GO composite. It is used to examine adsorbent materials' morphology and appearance. Figure 2a provides a lateral description of the synthesized material CaFe_2O_4 -GO composite. The CaFe_2O_4 particles are evenly dispersed onto the surface of the graphene oxide sheets, as represented in Figures 2b and 2c.

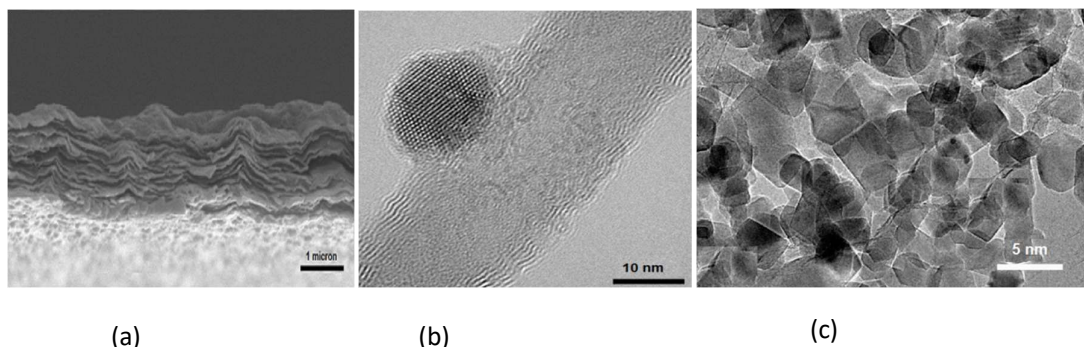


Figure 2. TEM image of (a, b and c) CaFe_2O_4 -GO composite

3.3 FESEM Analysis:

The SEM analysis can be used for analyzing morphology of the adsorbent. GO had a flat surface in the SEM image [39]. The FESEM image (Figure 3) made it evident that CaFe_2O_4 was placed on the graphene sheet. The graphene sheet separated the nanoparticles. In some cases, agglomeration occurred, which might be due to the magnetic properties of the prepared materials.

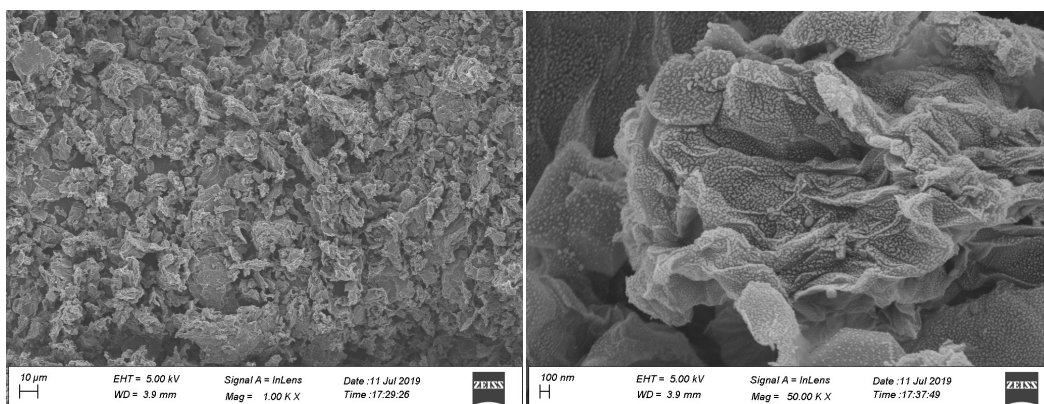


Figure 3. SEM image of $\text{CaFe}_2\text{O}_4\text{-GO}$ composite

4. Adsorption study:

4.1. Influence of pH on AB 25:

The pH of the solution represents one of the most essential variables in any process of adsorption. Adsorption of AB 25 is preferred at lower pH [44]. At this stage, more H^+ ions were available in the solution, which might be attracted by the partial negative charge of the adsorbate and develop the permanent positive site at the adsorbate molecule. Thus, the negative surface of the adsorbent (as indicated by the Zeta potential measurement) was found to attract the dye molecule more easily. Higher pH, however, causes the OH^- ion in the solution to attack the adsorbate molecule's partial positive site, minimizing its positive character and thus, its attraction for adsorbent sites, resulting in decreased adsorption (Figure 4).

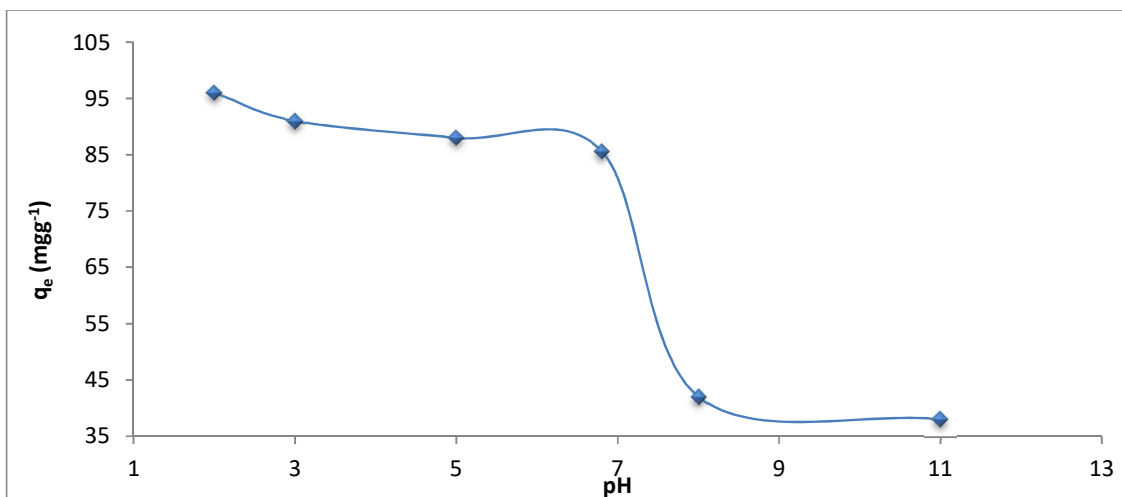


Figure 4: Influence of pH on adsorption at 303K

4.2. Influence of initial AB 25 dye concentration:

When the dye concentration varied from 10 to 30 mgL^{-1} , the amount of AB 25 dye absorbed per unit mass of adsorbent rose from 86.35 to 97.32 mgg^{-1} (Figure 5). More collisions between the dye molecule and the adsorbent's solid phase occur once the concentration of dye is increased. since this increases the driving power needed to overcome the dye's mass transfer resistance between the aqueous and solid phases. The unit mass of the adsorbents is exposed to a greater number of dye species at high dye concentrations, and as the proper binding

sites gradually fill up, an increasing number of dyes are absorbed. This increased the q_e despite a drop in net adsorption [45].

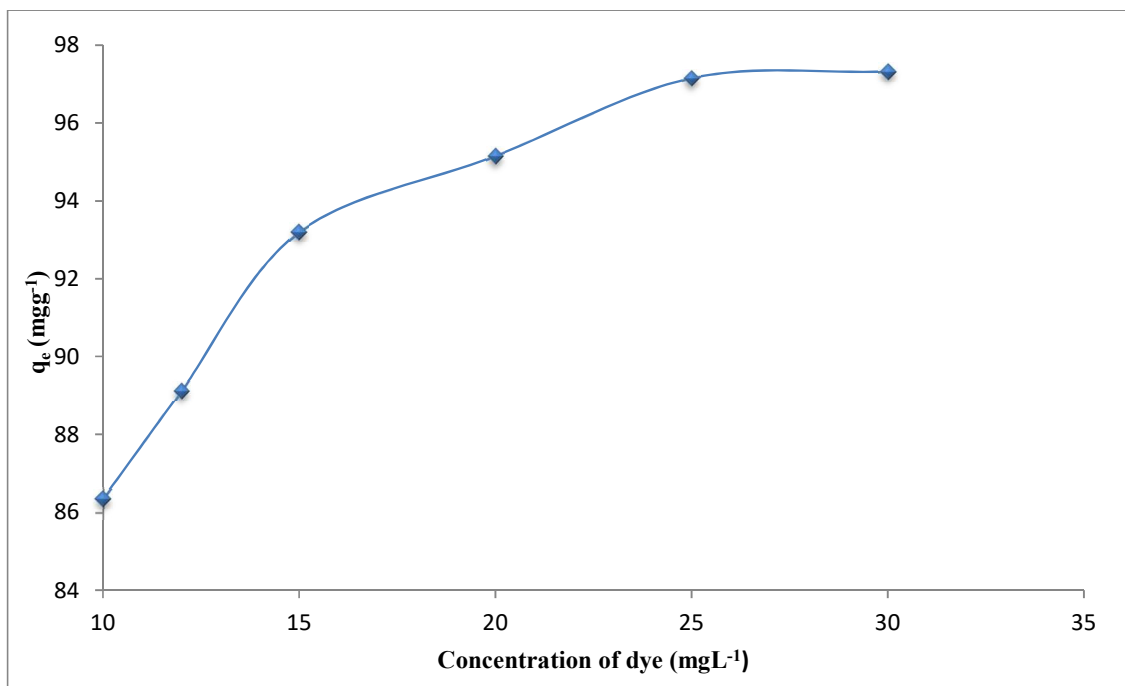


Figure5: The effect of initial AB 25 dye concentrations on CaFe₂O₄-GO composite at 303K

4.3. Influence of adsorbent load:

Figure 6 illustrates how variations in adsorbent load influence AB 25 removal. The amount of AB 25 absorbed per unit mass of the adsorbent (q_e) reduced from 81.21 to 54.56 mg g⁻¹ when the amount of adsorbent was increased from 0.02 to 0.18 gL⁻¹. On the other however, the degree of adsorption gradually increased from 16.24% to 98.17%. A decrease in electrostatic potential close to the solid surfaces and an increase in surface negative charge may be the cause of the higher percentage adsorption, which promotes adsorbent–adsorbate interaction.

The number of adsorption sites per unit mass decreased as a result of the unsaturation of the adsorption sites being successfully reduced by a significant amount of adsorbent. At the greater adsorbent quantity, this led to comparatively less adsorption, results decrease in adsorption density. Additionally, a modest quantity of adsorbent allowed the dye species to readily reach the adsorption sites, producing a high q_e value. The overcrowding of particles (triggered by the solid concentration effect) reduced the adsorptive capacity utilization of the adsorbent increase in adsorption per unit mass as the adsorbent load increased [46].

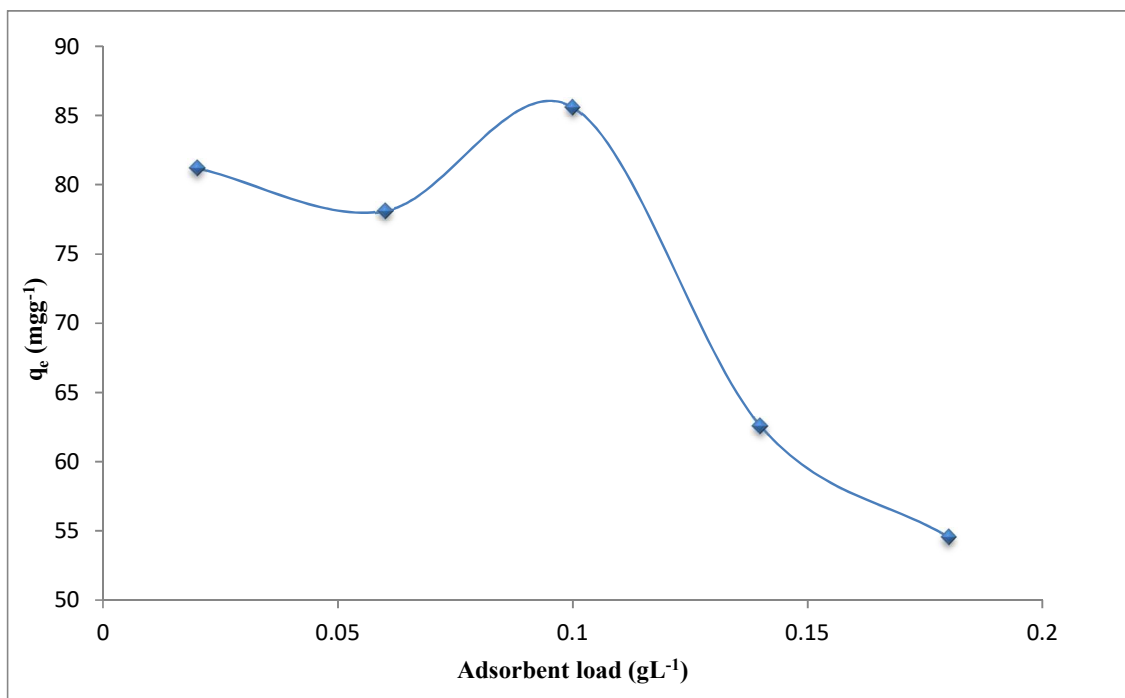


Figure 6: The effect of adsorbent load on adsorption of AB 25 dye at 303 K

4.4. Influence of time:

Figure 7 shows the effect of time on the adsorption of AB 25 by the CaFe_2O_4 -GO composite at room temperature (303 K). Adsorption increased at the beginning of the process and then slowed down after achieving equilibrium in 240 minutes. The largest amount of adsorption may have been achieved by the adsorbent's greater quantity of easily accessible active sites by making it possible for the dye molecule to stick to the adsorbent more successfully at the beginning. As time went on, fewer active sites became available, and the process reached equilibrium [47, 48].

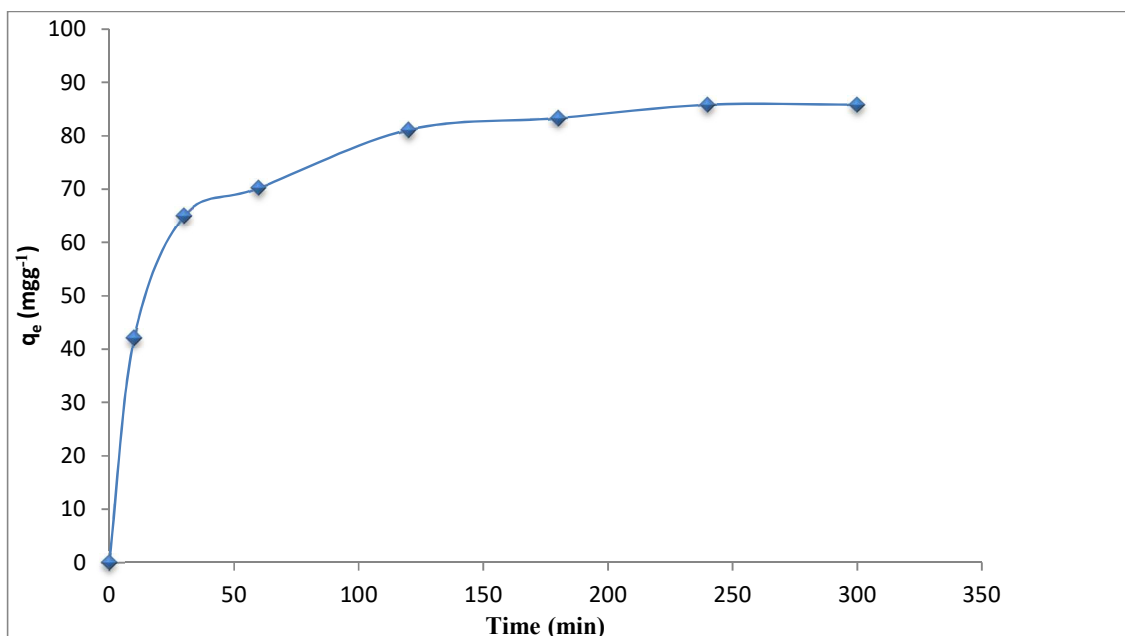


Figure 7: Amount of AB 25 dye adsorbed per unit mass (q_e) on CaFe_2O_4 -GO composites at different interaction time at 303 K

5. Adsorption isotherm:

5.1. Langmuir and Freundlich Isotherm:

An adsorption isotherm indicates how adsorption particles are distributed across the liquid and solid phases respectively. The adsorption isotherm for the adsorption of AB 25 on CaFe_2O_4 -GO composite at room temperature investigated for Langmuir [49]. The following equation corresponds to the linear expression of the Langmuir [50] equation

$$C_e/q_e = 1/(bq_m) + (1/q_m)C_e \quad (3)$$

Where, C_e implies the concentration of dye at equilibrium (mg L^{-1})

b represents the Langmuir constant

q_e implies the adsorption capacity at equilibrium (mg g^{-1}) and

q_m indicates Langmuir monolayer adsorption capacity (mg g^{-1}).

The plot of C_e/q_e vs C_e for on AB 25- CaFe_2O_4 -GO composites interaction was shown in the Figure 8 which suggests that adsorption follows Langmuir isotherms model.

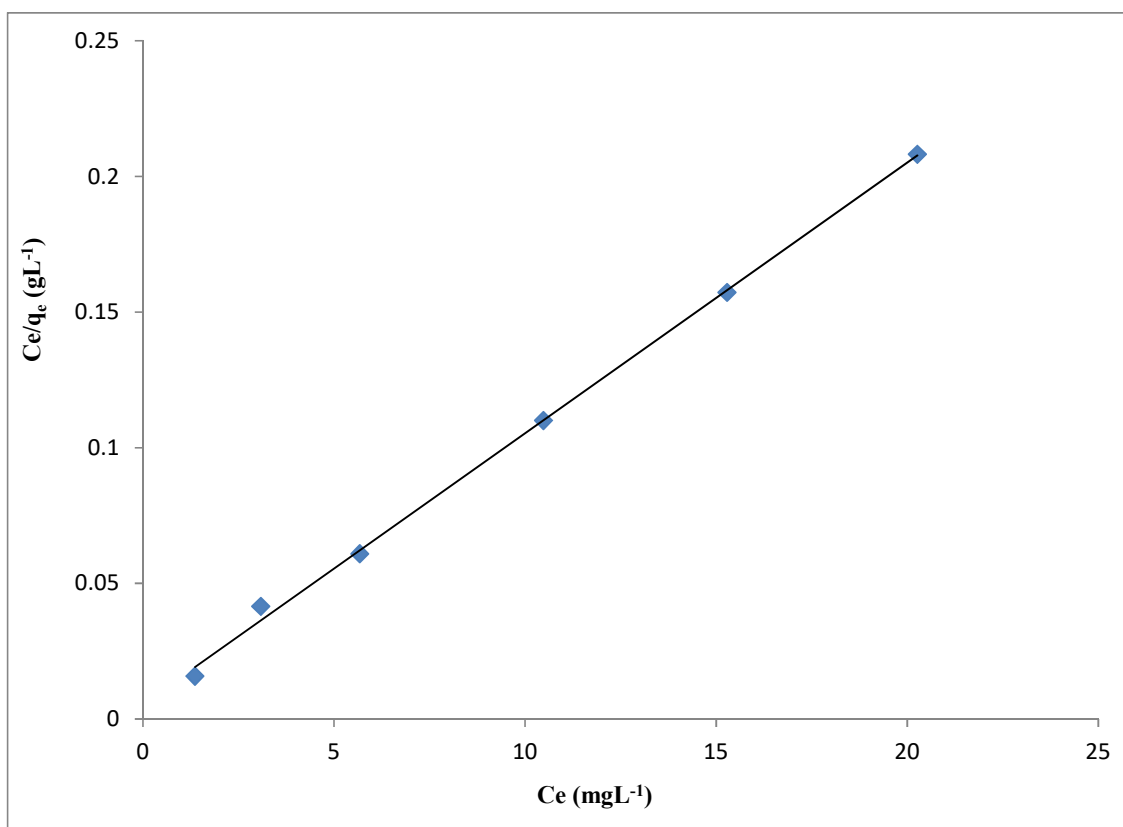


Figure 8: Langmuir plot for AB 25 dye adsorption at 303 K (Adsorbent 0.1 g L^{-1} , pH 6.8)

Freundlich isotherm suggests heterogeneous surface with multilayer adsorption [51] on to the surface of the adsorbent. Equation (4) gives the linear expression of the Freundlich [52] equation

$$\text{Log}(q_e) = \log k_f + (1/n) \log C_e \quad (4)$$

Where, k_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) represents the binding energy constant reflecting the affinity of adsorbent to dye, n indicates the Freundlich constant and C_e indicate the concentration of adsorbate at equilibrium (mgL^{-1}).

The plot of $\log q_e$ vs $\log C_e$ was shown in the Figure 9 at 303K which was found a straight line.

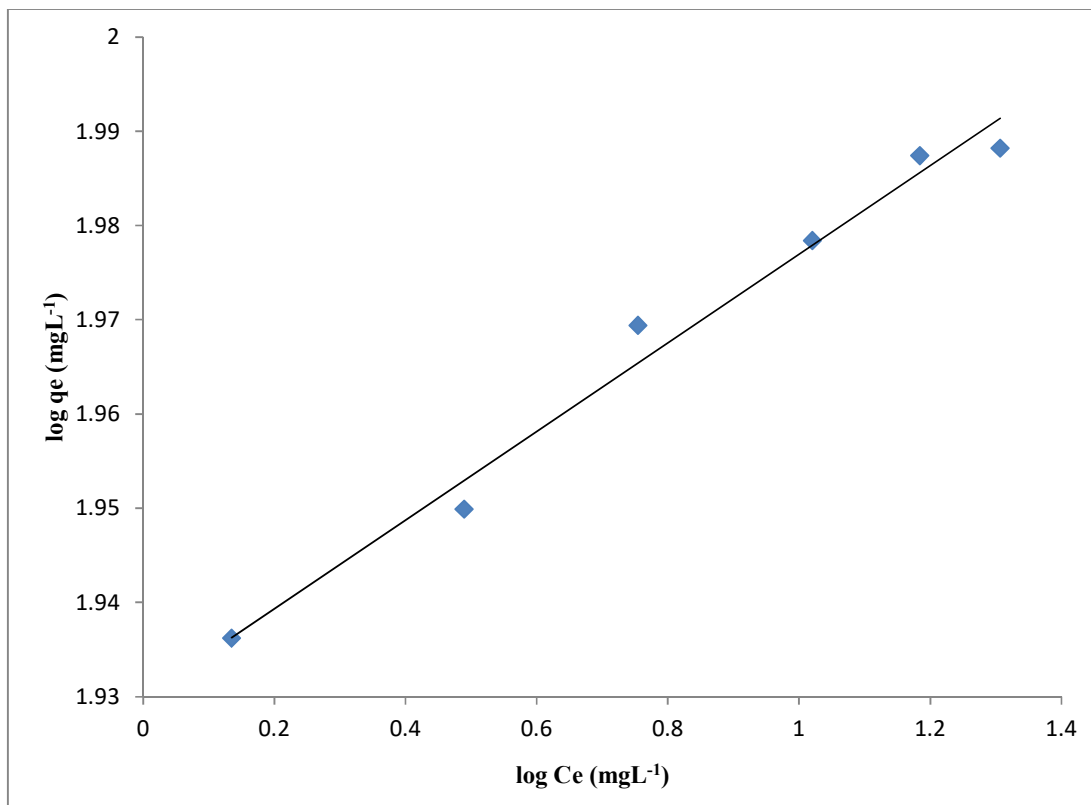


Figure 9: Freundlich plot for AB 25 dye adsorption (Adsorbent 0.1 gL^{-1} , pH 6.8, temperature 308 K)

Figures 8 and 9 were employed to calculate the Langmuir and Freundlich isotherm parameters, which are depicted in Table 2. It was evident from the plots and the regression coefficient values (R^2) that the Langmuir isotherm model better fits than the Freundlich. This confirms the homogenous nature of the adsorbent with monolayer deposition of adsorbates onto its sorption sites [53]. The Langmuir capacity of adsorbent for the adsorption of AB 25 was 100 mgg^{-1} with regression coefficient (R^2) 0.998. The value of regression coefficient (R^2) was quite close to the unity and the process of removal of AB 25 dye followed both the Freundlich and Langmuir isotherms [54], however the Langmuir isotherm model was more appropriate for the experimental data.

Table 2: The parameters obtained at 303 K using the Freundlich and Langmuir isotherm models.

Langmuir Isotherm	Freundlich Isotherm
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q_m	100 mgg ⁻¹	n	21.28 mg ^{1-1/n} L ^{1/n} g ⁻¹
b	2.0	K_f	84.91
R^2	0.998	R^2	0.982

6. Kinetics study of the adsorption mechanism:

6.1. Pseudo-first and second-order kinetics:

The Lagergren pseudo first order and second order integrated model can be applied for the kinetics and adsorption mechanism [55, 56] which shown in the equation (5) and (6).

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (5)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (6)$$

Where q_e and q_t represent the amounts of adsorbed per unit mass at equilibrium (mg g⁻¹) and any time t (min) in the adsorption process respectively. K_1 (min⁻¹) indicates the rate constant for pseudo first order kinetics and K_2 (g mg⁻¹ min⁻¹) represent the rate constant for second order kinetics model. A straight line must show up on the plot $\log(q_e - q_t)$ vs. t plot for pseudo first order kinetics. This curve was linear (Figure 10) and the rate constant, K_1 was 1.61×10^{-2} min⁻¹ (Table 3). The Lagergren plots' q_e values as well as the experimental q_e values were over 52.02% different. Thus, the rate processes were less likely to be explained by first order kinetics. Again the plots of t/q_t vs. t (figure 11) was linear ($R^2 = +0.999$) with the rate constant, K_2 was found 8.49×10^{-4} gmg⁻¹ min⁻¹ at 303 K. The pseudo-second-order was the best-fit kinetic model, indicating that the binding interaction between adsorbent and dye was not completely physical but also included some chemical interaction to some extent.

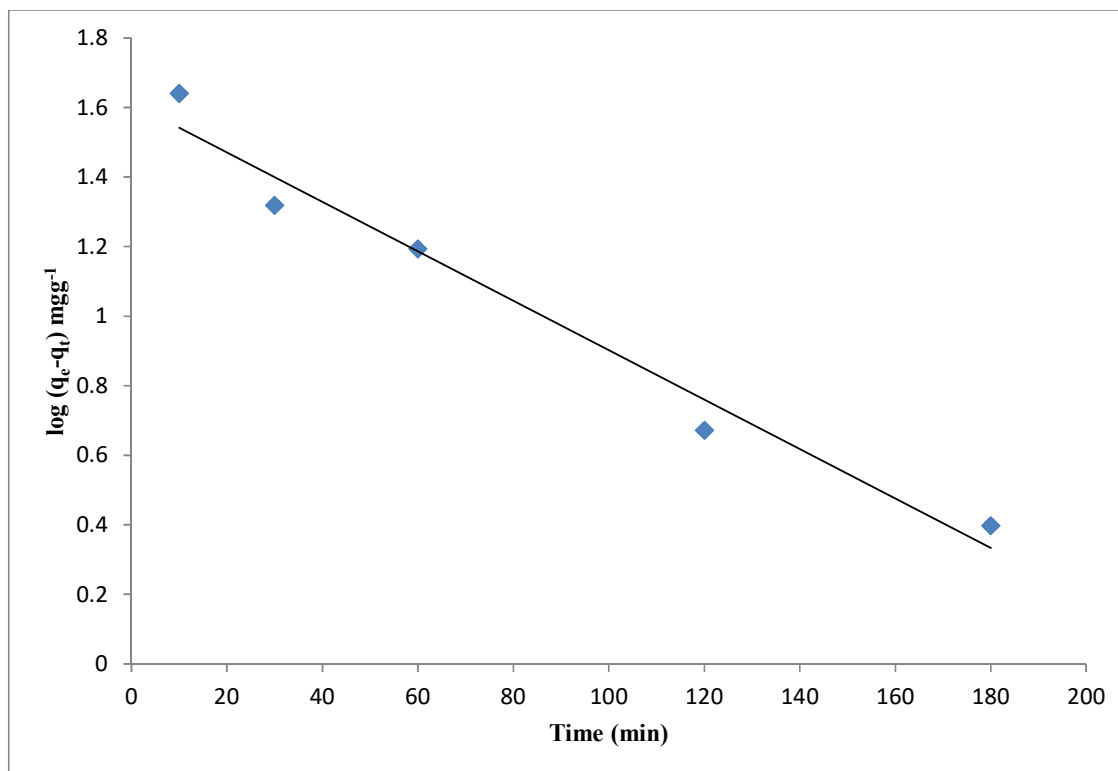


Figure 10: Lagergren first order plot for AB 25 dye adsorption at 303 K (Adsorbent 0.1 gL⁻¹, AB 25 10 mgL⁻¹, pH 6.8)

Table 3: Rate coefficient, Experimental and Calculated q_e values from Lagergren and second order plots for adsorption of AB 25 on to CaFe₂O₄-GO composites at temperature 303 K.

Lagergren first order rate coefficient		Second order rate coefficient	
K_1	$1.61 \times 10^{-2} \text{ min}^{-1}$	K_2	$8.49 \times 10^{-4} \text{ gm}^{-1} \text{ min}^{-1}$
R^2	0.972	R^2	0.999
q_e (calculated)	41.02	q_e (calculated)	90.90
q_e (Exp.)	85.8	q_e (Exp.)	85.8
Deviation	52.02 %	Deviation	5.94 %

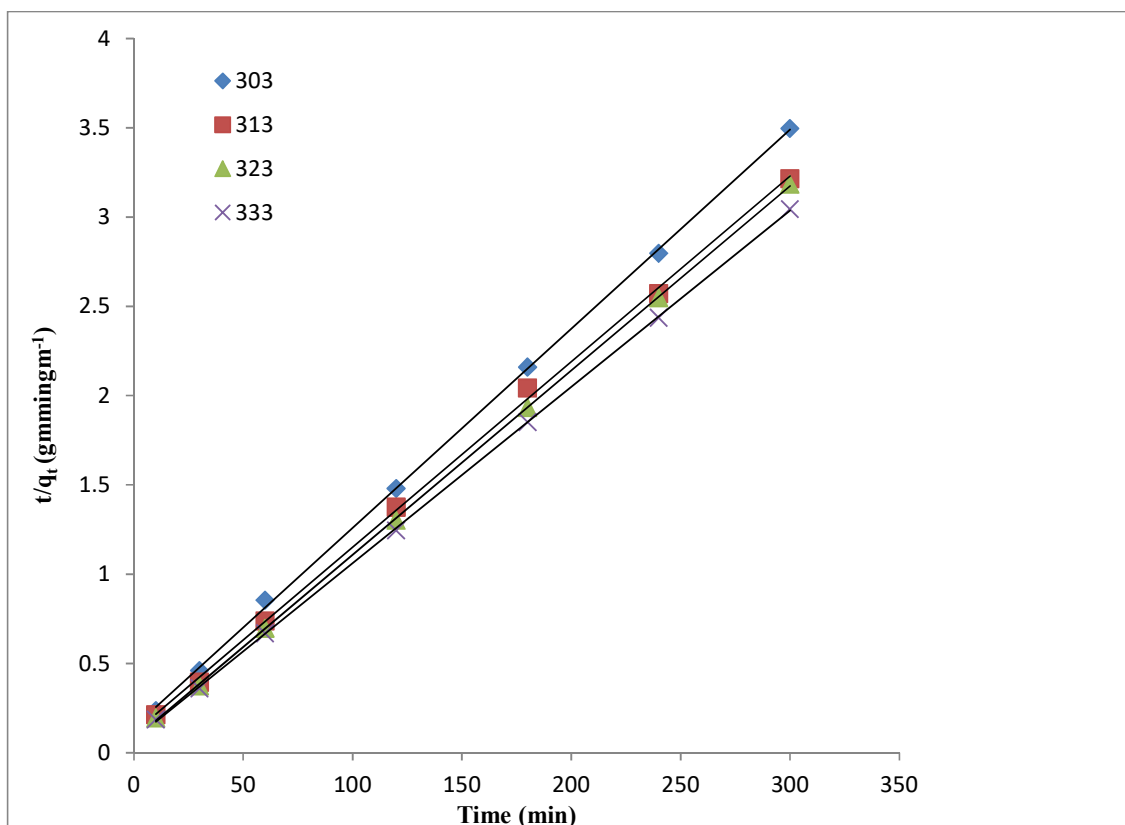


Figure 11: Second order plot for AB 25 dye adsorption at (303-333) K (Adsorbent 0.1 gL⁻¹, AB 25 10 mgL⁻¹, pH 6.8)

A comparison of q_e values (experimental and those obtained from the second order plots) indicated that the adsorption was preferably takes place in second order kinetics. Table 4 showed the variety of information acquired from the pseudo second order model at various temperatures (303-333K).

Table: 4. Pseudo Second order kinetic parameters for the AB 25 adsorption at different temperature (CaFe₂O₄-GO composites- 0.1gL⁻¹, dye concentration 10 mgL⁻¹, pH 6.8)

Temperature (K)	K ₂ (gmg ⁻¹ min ⁻¹)	q _{e,cal} (mgg ⁻¹)	q _{e,Exp} (mg g ⁻¹)	Deviation(%)	R ²
303	8.49 x 10 ⁻⁴	90.90	85.8	5.94	0.999
313	8.85 x 10 ⁻⁴	100	93.3	7.18	0.999
323	9.52 x 10 ⁻⁴	103	95.2	8.19	0.999
333	11.09 x 10 ⁻⁴	111	98.5	12.7	0.999

6.2. Elovich equation:

The following is the Elovich equation [57], which is used for chemical interactions of heterogeneous solid surfaces.

$$q_t = \beta \ln(\alpha\beta) + \ln t \quad (7)$$

where α and β represent the Elovich coefficient. The plot of q_t vs. $\ln t$ from Figure 12 may be used to find the value of the Elovich coefficient. The value of adsorptive coefficient, α and desorption coefficient, β were 50.14 g mg⁻¹min⁻² and 7.9 x 10⁻² mg g⁻¹ min⁻¹ respectively with R² value ~0.956, which was relatively low value.

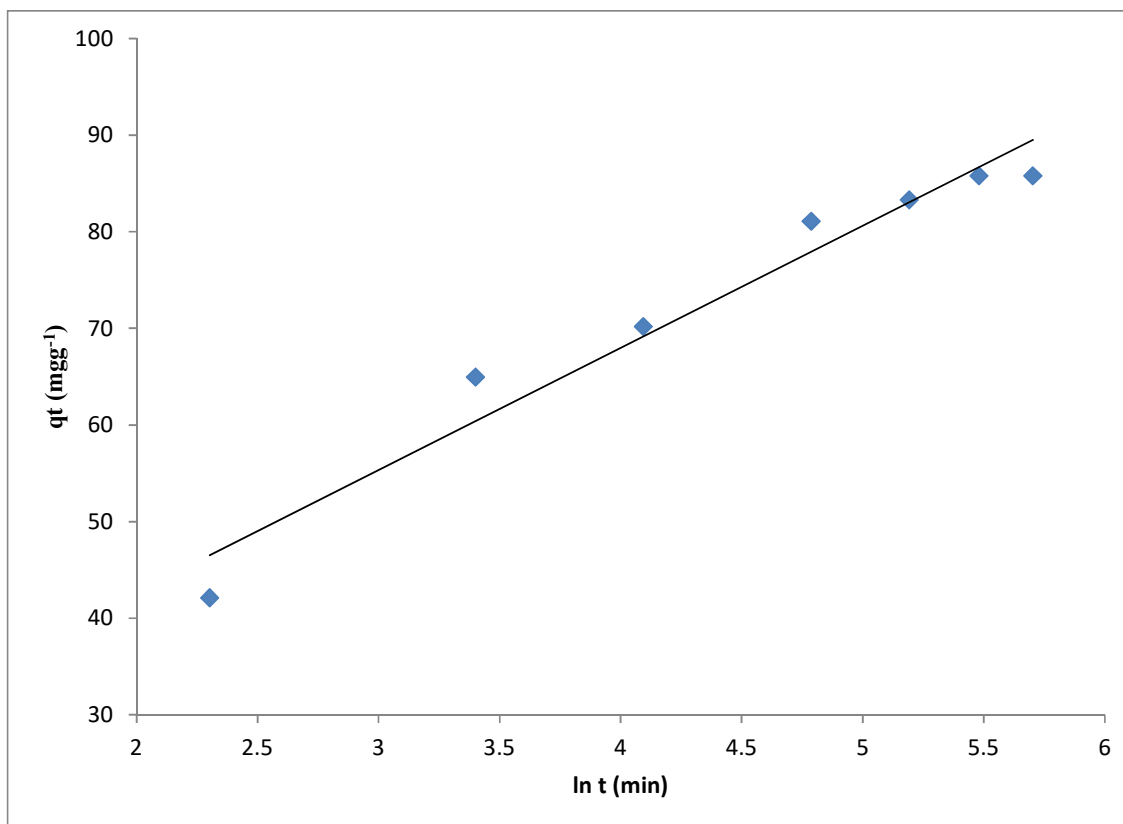


Figure 12. Elovich plot for AB 25 dye adsorption at 303 K (Adsorbent- 0.1g^L⁻¹, AB 25 10 mgL⁻¹, pH 6.8)

6.3. Intra particle diffusion:

Weber and Morris for the adsorption process [58] give the information of porous materials and given by the following relation

$$q_t = k_i t^{0.5} + C \quad (8)$$

where k_i implies the internal diffusion constant (mg g⁻¹ min^{-0.5}) and q_t implies the amount of adsorbate adsorbed at any time t (min). The intercept of a graph of q_t vs. $t^{0.5}$ curve could be applied to determine the k_i and C values. The k_i value was 2.755 mg g⁻¹ min^{-0.5} and C was 44.37. The obtained linear portions of the curves did not pass through the origin (Figure 13) indicating that the mechanism of AB 25 dye removal on CaFe₂O₄-GO composite was not followed solely by inter-particle diffusion although the possibility was not fully ruled out.

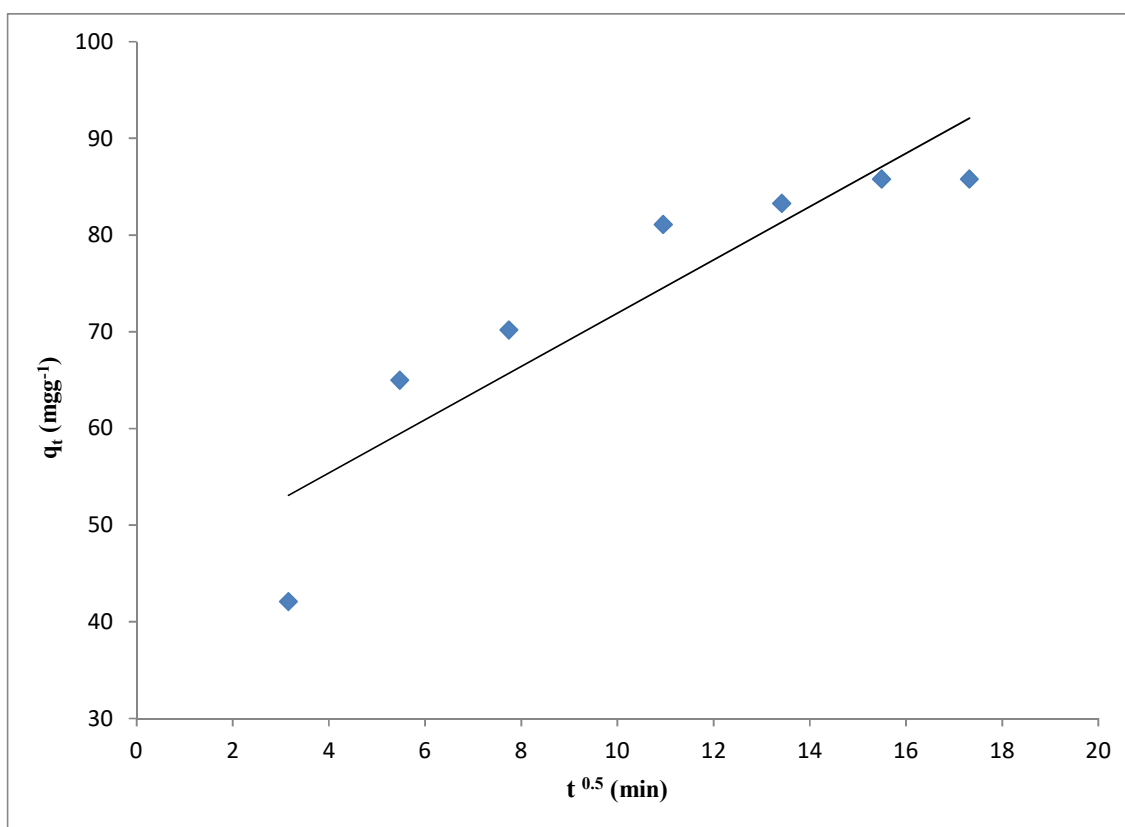


Figure 13: Intra particle diffusion plot for AB 25 adsorption at 303 K (Adsorbent 0.1 gL⁻¹, AB 25 10 mgL⁻¹, pH 6.8)

6.4. Liquid film model:

The following is the equation describing the liquid film diffusion model [59]

$$\ln(1 - q_t/q_e) = -k_d t \quad (9)$$

Where k_d (min⁻¹) is a rate parameter. The curve is linear with R^2 value +0.972, the intercept is 0.739 (Figure 14). The resulting curve did not cross the origin, but the intercept was quite near zero, implying that diffusion from the liquid phase may be more significant than the intraparticle diffusion model. The k_d value was 0.016 min⁻¹

indicating that the liquid film diffusion might play some important roles in the overall AB 25 dye adsorption mechanism.

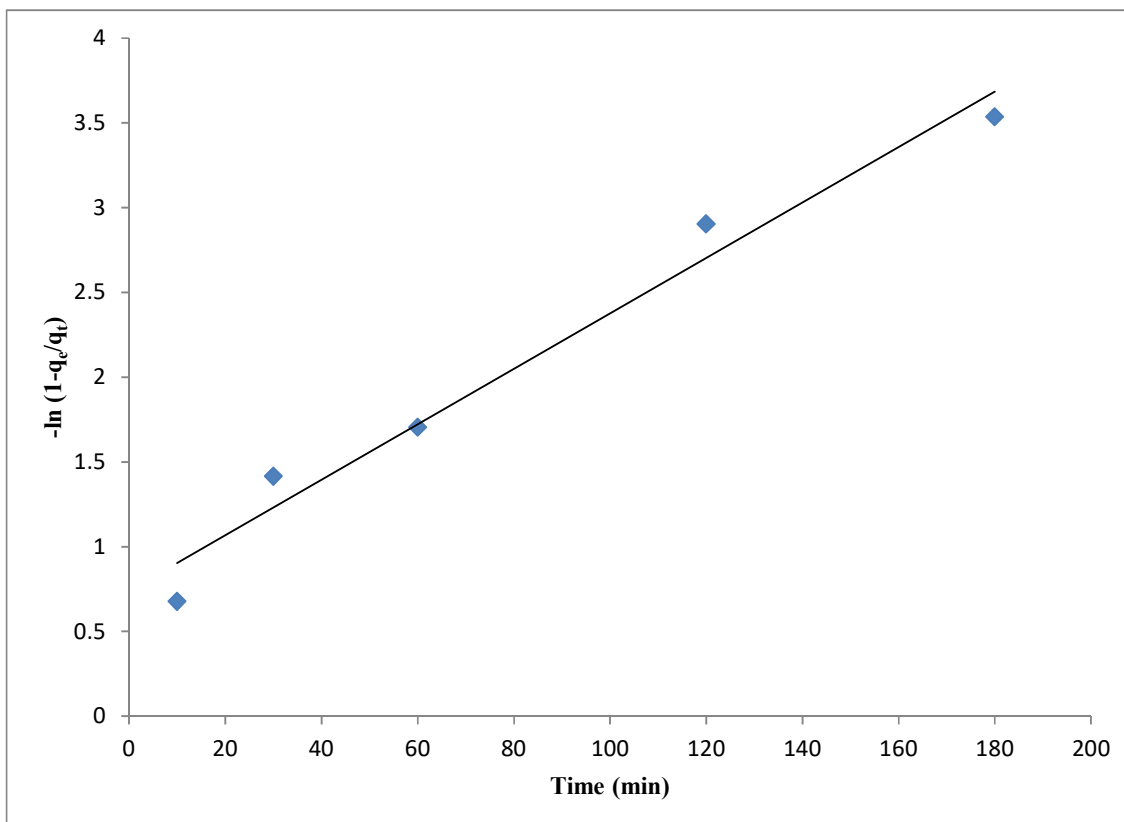


Figure 14: Liquid film diffusion plot for AB 25 dye adsorption at 303 K (Adsorption 0.1 gL^{-1} , AB 25 10 mgL^{-1} , pH 6.8)

7. Influence of Temperature and adsorption thermodynamics:

The interaction between the adsorbent, $\text{CaFe}_2\text{O}_4\text{-GO}$ composite and AB 25 dye was in the range of 303 K to 333 K which indicated the process was endothermic in nature. The percentage of adsorption rises as the temperature rise from 303K to 333K (Figure 15). This might be attributed to an increase in the number of active sites accessible for adsorption and an increase in ion mobility with temperature.

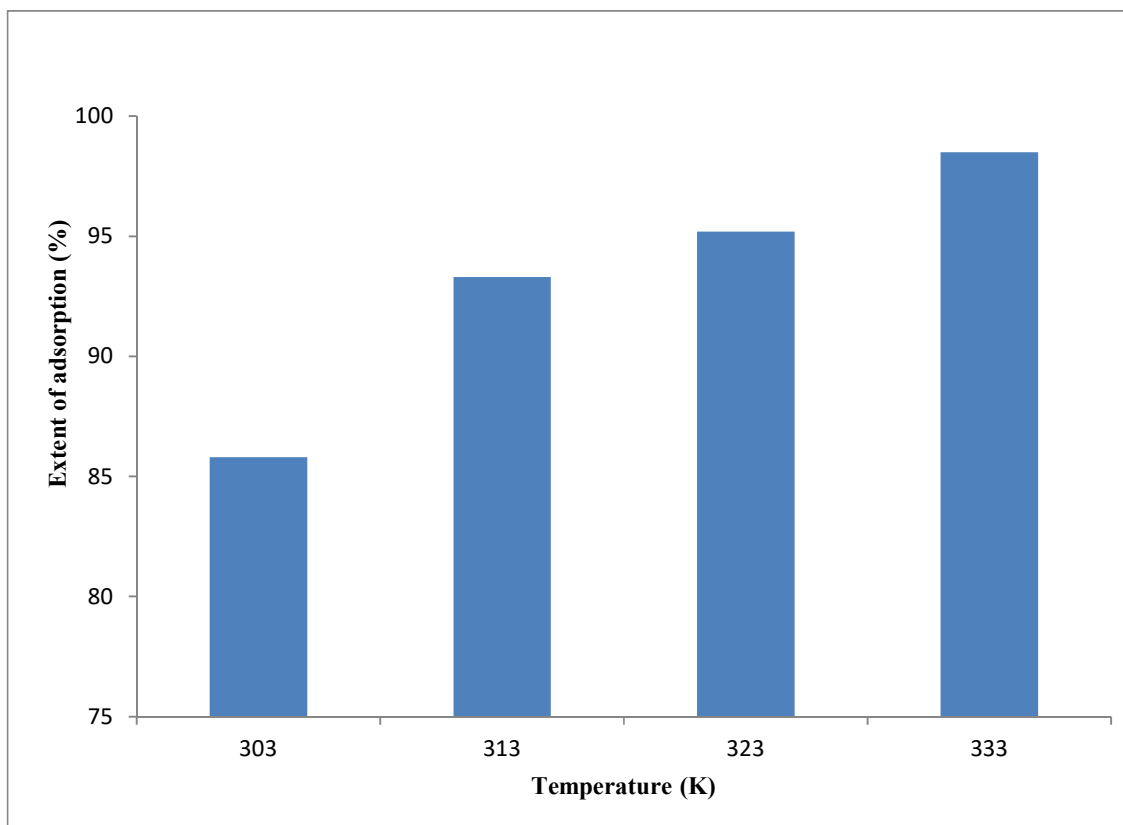


Figure 15: The percentage of adsorption of AB 25 dye concentration (mgL^{-1}) at different temperature (303-333K)

The following expression was used for calculating the thermodynamic parameters ΔH , ΔS , and ΔG .

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Where K_d (q_e/C_e) is the distribution coefficient, T implies the temperature (K), Ideal gas constant R ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$). ΔH and ΔS represents the change in enthalpy and change in entropy respectively. ΔG represent the change in Gibbs free energy. The plot for $\ln K_d$ vs. $1/T$ was employed to determine ΔH and ΔS .

In the present work, the positive ΔH indicated the endothermic behaviour of the adsorbate-adsorbent system (Table 6). The positive value of change in entropy, ΔS , indicated the increase of entropy with increase in temperature, which suggested the adsorption process was favourable for AB 25 dye adsorption. The negative ΔG value, in conjunction with an increase in temperature indicated that the adsorption process was favourable. The change of Gibbs free energy, ΔG , in the range of -20 to 0 kJ mol^{-1} , indicated physical adsorption [60, 61, 62].

The Arrhenius equation expressed as,

$$K = A \exp^{-E_a/RT} \quad (12)$$

$$\ln k = \ln A - E_a/RT \quad (13)$$

Where k ($\text{g mg}^{-1} \text{ min}^{-1}$) represent the pseudo second-order rate constant, A ($\text{g mg}^{-1} \text{ min}^{-1}$) represent the frequency factor, E_a (kJ mol^{-1}) represent the activation energy for adsorption, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is called the gas constant,

and T is the temperature in the Kelvin scale. The linear fitting curve was obtained by plotting $\ln k$ vs $1/T$ (Figure 16), and the activation parameters were found from the slope and intercept. The activation energy, E_a , for the process was found to be $9.186 \text{ KJ mol}^{-1}$, which signified the process might be physically controlled [56,63].

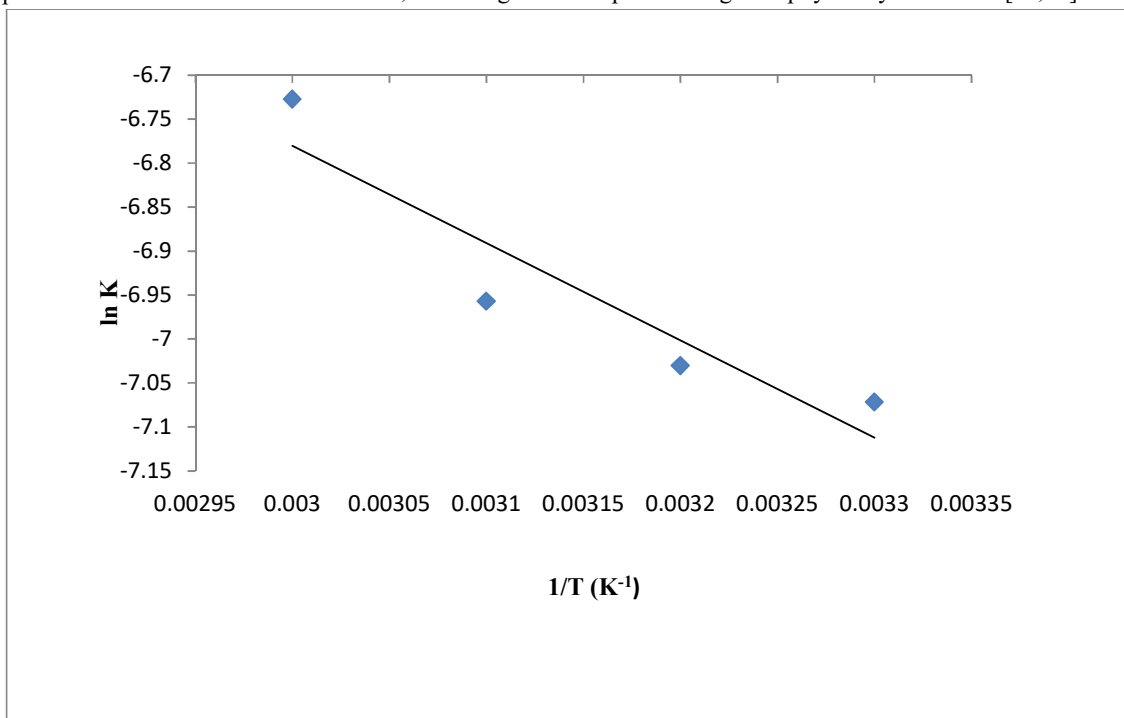


Figure 16: Arrhenius plots illustrating the adsorption of AB 25 dye on a CaFe_2O_4 -GO composite

Table: 6. Thermodynamic data for adsorption of AB 25 on CaFe_2O_4 -GO (CaFe_2O_4 -GO Composite – 0.1 gL^{-1} , dyeconcentration 10 mgL^{-1} , pH6.8 time 240 minute; ΔH , ΔS , ΔG and E_a are kJ mol^{-1} , $\text{J K}^{-1} \text{ mol}^{-1}$, kJ mol^{-1} , kJ mol^{-1} respectively)

ΔH	ΔS	E_a	ΔG			
			303 K	313 K	323 K	333 K
60.7	234.039	9.186	-10.202	-12.542	-14.882	-17.222

8. Comparison of Langmuir interaction with some other adsorbent:

A comparison of Capacity of Langmuir monolayer interactions of various adsorbent for adsorption of AB 25 dye is depicted in Table 5.

Table 5: Comparison of Langmuir monolayer adsorption capacities of AB 25 adsorption onto the surface of the different adsorbents.

Adsorbent	$q_m (\text{mgg}^{-1})$	Experimental Temperature (K)	References
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Hazelnut	60.2	293	[48]
Peat	14.4	291	[57]
Diatomite	21.41	298	[66]
Saw dust-walnut	36.9	293	[48]
Zeolite	64.2	303	[67]
CaFe ₂ O ₄ -GO composite	100	303	This work

9. The reusability study:

Several adsorption-desorption cycles in the ethanol/acetic acid solution were conducted to test the reusability of CaFe₂O₄-GO Composite. After vigorous stirring for roughly ten hours at room temperature using a magnetic stirrer, the adsorbed AB 25 dye was removed from the ethanolic/acetic acid solution in each cycle. The percentage of adsorption of the CaFe₂O₄-GO composite for AB 25 dye following three rounds of adsorption was displayed in Figure 17. The CaFe₂O₄-GO composite's initial adsorption percentage for AB 25 was found to be 86.5%. The percentage of adsorption of the CaFe₂O₄-GO composite for AB 25 dye lowered as the number of adsorption cycles increased. At the fourth cycle, the CaFe₂O₄-GO composite's dye adsorption percentage was found to be 79.3%.

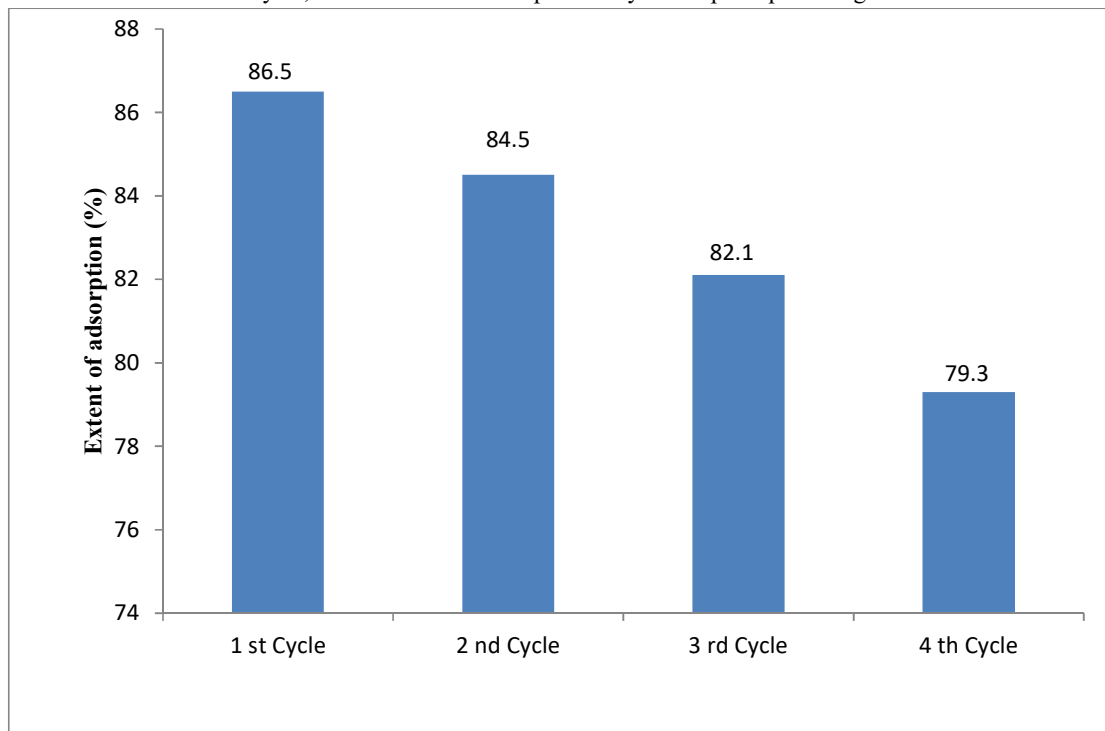


Figure 17. Reusability of CaFe₂O₄-GO composite on successive use for adsorption of AB25 dye

10. Conclusion:

In this work we successfully synthesized the CaFe_2O_4 -GO composite and was used to remove AB 25 toxic dye from aqueous solution. The adsorption was preferably followed by Langmuir isotherm over Freundlich isotherm with monolayer adsorption capacities 100 mg g^{-1} . The change in enthalpy was a positive quantity, which suggested the adsorption process was endothermic in nature. The percentage of adsorption increased with rise in temperature. The adsorption process more effectively followed the second-order kinetic model. Removal of AB toxic dye from water by this adsorbent was dependent on the pH of the medium of the solution. The process was governed by the decrease in Gibbs free energy. The thermodynamic study indicated that the adsorption process was both spontaneous and of a physical nature. The Graphene calcium ferrite nanocomposite was a promising adsorbent which was suitable to remove AB 25 toxic dyes from aqueous solutions due to its reusability.

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