

Synthesis and Characterization of Graphene Oxide Nano-sheets for Effective Removal of Copper Phthalocyanine from Aqueous Media

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ABSTRACT: Graphene Oxide (GO) nano sheets was synthesized from graphite by Hummers method. The nature and morphology of the GO were characterized using FTIR, UV-Vis, SEM and XRD analysis. Batch sorption experiments were carried out to remove copper (ii) phthalocyanine-tetrasulfonic acid tetrasodium salt $[\text{Cu}(\text{tsPc})^{4-}.4\text{Na}^+]$ from its aqueous solutions using GO as an adsorbent. Experiments were carried out to investigate the influence of contact time, initial dye concentration, ionic strength, and temperature on the adsorption performance. The Langmuir and Freundlich isotherm models have been applied and the Freundlich model was found to be fit with the equilibrium isotherm data. The kinetic data were analyzed using pseudo first-order and pseudo-second-order models. The adsorption kinetics matched well with the pseudo-second-order kinetic model. The thermodynamic analysis showed that the adsorption process is spontaneous and endothermic. The experiments showed that GO is very good adsorbent with high adsorption capacity for $[\text{Cu}(\text{tsPc})^{4-}.4\text{Na}^+]$ dye and the main reason for this good affinity of dye onto GO can be π - π stacking interactions between the polycyclic aromatic structure of (CuTSPc) and unsaturated bonds on the surface of graphene oxide.

KEYWORDS: Waste water treatment; Graphene oxide; Copper Phthalocyanine; Adsorption.

INTRODUCTION

The control of water pollution has become of increasing importance in recent years. The release of dyes into the environment constitutes only a small proportion of water pollution, but dyes are visible in small quantities due to their brilliance. There are more than 100,000 commercially available dyes with over 7×10^5 ton of dye-stuff produced annually and There are many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes. Many of these dye wastes are toxic and even carcinogenic and

this poses a serious hazard to aquatic living organisms and as a result, many governments have established environmental restrictions with regard to the quality of colored effluents and have forced dye-using industries to decolorize their effluents before discharging. Currently, removal of dyes from effluents is by physio-chemical means. There is a need to alternative treatments that are effective in removing dyes from large volumes of effluents and are low in cost [1-3].

A range of treatment technologies such as trickling filters, active sludge, chemical coagulation, photo degradation,

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adsorption with different materials, membrane filtration, and so forth has been studied extensively for dye removal over the years. Though a number of processes are available for dye removal from aqueous system, adsorption is getting special interest from the researchers worldwide due to its high efficiency, cost effectiveness, and simple operation process [4].

Approximately 25% of all artificial organic pigments are phthalocyanine derivatives. Because of low solubility of Copper phthalocyanine (CuPc) dyes in water (less than 1 mg/l) they are produced by introducing solubilizing groups, such as one or more sulfonic acid functions. These dyes find extensive use in various areas of textile dyeing (Direct dyes for cotton), for spin dyeing and in the paper industry. Metal phthalocyanines have long been examined as catalysts for redox reactions [5-8]. Areas of interest are the oxygen reduction reaction and the sweetening of gas streams by removal of hydrogen sulfide [9]. There is evidence that exposure to phthalocyanines can cause serious birth defects by copper depletion in developing embryos [10]. So, finding new sorbent for their removal from waste water is necessary. Recent works have shown that graphene oxide is a good adsorbent with large adsorption capacity for removing dyes from waste water such as methylene blue [11-16].

This work investigates the adsorption behavior of copper phthalocyanine-3,4,4',4''-tetrasulfonic acid tetrasodium salt $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ (shown in Fig. 1) onto graphene oxide nanosheets that synthesized by hummers method in order to modeling of this process for treatment of refineries waste water.

EXPERIMENTAL SECTION

Materials

Natural Graphite flakes (100 meshes) and copper phthalocyanine-3,4,4',4'' tetrasulfonic acid tetra- sodium salt $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ were obtained from Sigma-Aldrich (Steinheim, Germany). Potassium permanganate, sodium nitrate, hydrochloric acid, sodium hydroxide and hydrogen peroxide obtained from Merck company (Germany).

Preparation of Graphene Oxide

Graphene oxide was synthesized from graphite by *Hummers* method [17,18]. 2 g of graphite powder was mixed with a mixture of 120 mL sulfuric acid (98 wt%),

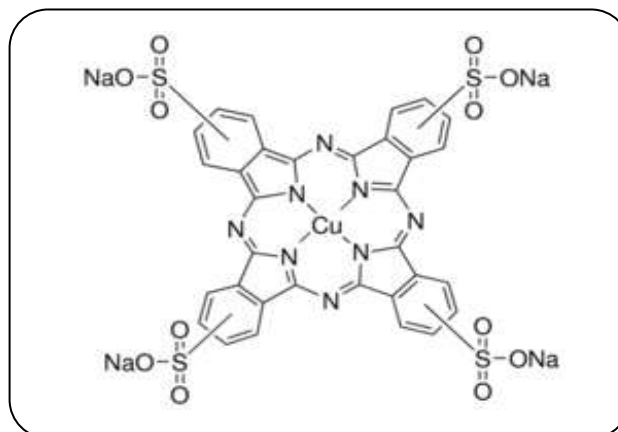


Fig. 1: $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ salt structure.

potassium permanganate (12 g) and sodium nitrate (1 g) in ice bath. The ice bath was then removed and the resulting mixture was stirred at 308 K until it became pasty brownish and then slowly diluted with deionized water. Then, 30% H_2O_2 was added to the mixture causing the color turning to yellow along with bubbling. The mixture was centrifuged and washed with 10% HCl solution to eliminate residual metal ions. After filtration and drying at 298 K for 3 days in a vacuum oven, Graphene Oxide (GO) was obtained.

Characterization of adsorbent

Functional groups on the surface of graphene oxide were analyzed by a Bruker (alpha) FT-IR spectrometer within the wave range $400\text{--}4000\text{ cm}^{-1}$ and the Morphology of graphene oxide were characterized by FESEM (Sigma, Zeiss). The UV-Vis absorption spectra of graphene oxide aqueous solution were collected using a UV-Visible spectrophotometer (Perkin Elmer lambda 45). X-Ray Diffraction (XRD) measurements were conducted using an INEL Equinox 3000 X-ray diffractometer with Cu K α radiation ($\lambda=1.5418\text{ \AA}$).

Adsorption experiments

Batch adsorption experiments were carried out in 50 mL glass containers with constant stirring under ambient conditions and neutral pH. A stock solution of $\text{Cu}(\text{tsPc})^{-4}$ (1000 mg/L) was prepared and further diluted to the required concentrations. 0.005 g adsorbent (GO) and 10 mL aqueous solution of dye with predetermined concentrations (300-700 mg/L) were placed in a 50 mL flask to evaluate the initial concentration effect on

adsorption process. The effect of temperature on the adsorption of dye was studied by agitating 10 mL of 700 mg/L solution of $\text{Cu}(\text{tsPc})^{-4}$ in a thermostatic bath (298, 303, 313 and 323 K). the effect of ionic strength investigated at room temperature with the various concentration of NaCl (0 to 0.2 mol/L).

After adsorption equilibrium and centrifuging the resulting solution for 2 min, the concentration of dye in the solution was measured using a UV-visible spectrophotometer (Perkin Elmer lambda 45 model) at a maximum wavelength (λ_{max}) of 661 nm. the amount of adsorbed dye at equilibrium q_e (mg/g) was calculated from the following equation [19]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations of dye in solution (mg/L), V is the volume of solution (L) and W is the mass of adsorbent (g).

Adsorption kinetics of dye

The effect of contact time on the adsorbed amount of dye was investigated at a 500 mg/L initial concentration of $\text{Cu}(\text{tsPc})^{-4}$. 0.002 g of graphene oxide was introduced into a flask containing 10 mL of dye solution and it was stirred as a function of time. At various time intervals, samples were taken and the dye concentration remaining in solution was measured after centrifugation. The amount of dye adsorbed on adsorbent at time t , q_t (mg/g), was calculated by using the following equation [20]:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where q_t and C_t are the adsorption capacity (mg/g) and the concentration of dye solution (mg/L) at time t , respectively.

RESULTS AND DISCUSSION

Characterization of graphene oxide

Fig. 2.a shows the FESEM image of synthesized Graphene oxide. The GO presents the sheet-like structure with the large thickness (not few layer GO), smooth surface, and wrinkled edge.

The FT-IR spectrum of GO (Fig. 2.b) reveals the presence of functional groups such as carboxyl, phenolic, epoxy, and hydroxyl groups. The bands at 1625

and 1720 cm^{-1} are attributed to phenol C=C ring stretching and carbonyl groups, respectively. band in 1223 cm^{-1} should be belong to epoxide functional group. Broad band at 3423 cm^{-1} confirms presence of hydroxyl groups.

The UV-Vis spectrum of graphene oxide in water (Fig. 2.c) shows absorption peaks at 230 nm. This absorption peak is near 265 for graphene because of its more conjugated unsaturated bonds.

XRD pattern (Fig. 2.d) shows that With graphite being oxidized to graphene oxide, the sharp reflection of graphite at $2\theta = 26.47^\circ$ disappears, and a new peak at $2\theta = 10.15^\circ$ that corresponds to graphene oxide appears. The GO interlayer spacing (d) calculated according to the Bragg's law. Changing 0.33 nm for graphite to 0.87 nm for graphene oxide shows a good oxidation degree for graphite during the synthesis.

Effects of adsorption time and initial dye concentration

The amount of adsorbed dye increased with an increase in adsorption time and then reached equilibrium and stayed constant. The reason is existence of more active sites in comparison with dye ions in first minutes of adsorption and when most of these sites are saturated, the adsorption amount becomes constant (Fig. 3). After 45 minutes, there is not significant increase in q_e , so 45 min. chose as equilibrium time for other experiments. This equilibrium time was constant for each initial dye concentrations. Also the effect of initial concentration on the uptake of dye was studied at different concentration of $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ by keeping other parameters constant. As shown (Fig. 4), the amount adsorbed increases with increasing initial dye concentration. This is because of the initial concentration provides driving force for mass transfer between the aqueous and solid phases.

Effect of salt concentration on adsorption

The wastewater containing dye has commonly higher salt concentration, and effect of ionic strength (or salt concentration) is of some importance in the study of dye adsorption onto adsorbents. It was seen that the increase in the salt concentration resulted a partially decrease in dye adsorption (Fig. 5). This trend indicates that the adsorbing efficiency decreases when NaCl concentration increased in the dye solution, which could be attributed to the competitive effect between $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ ions and

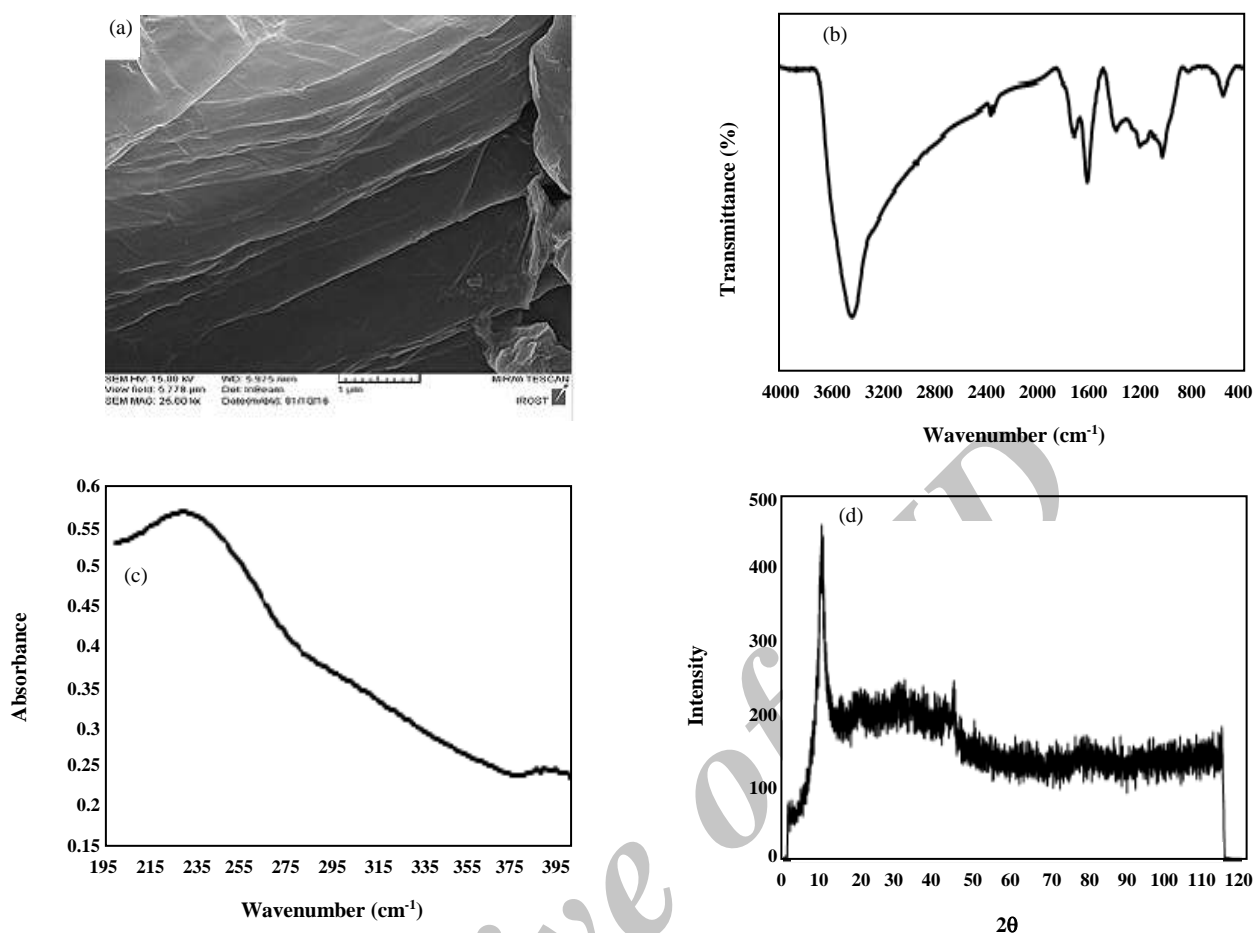


Fig. 2: (a) FESEM; (b) FT-IR; (c) UV-Vis; (d) XRD analysis of synthesized Graphene Oxide.

negative or positive charged ions from the salt for the sites available for the adsorption process.

Effect of temperature

The effect of temperature on the adsorption of $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^{+}]$ onto GO is shown in (Fig. 6.a).

It showed that higher temperature facilitated the adsorption capacity, which indicating that adsorption process is endothermic. This is mainly because of changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. Also with increasing the temperature, viscosity of the solution decreases and the rate of diffusion of dye molecules will increase.

In order to understand the effect of temperature on the adsorption process, thermodynamic parameters

should be determined at various temperatures. For this reason, three basic thermodynamic parameters, the Gibbs free energy of adsorption (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS) were studied. These thermodynamic parameters for this adsorption process were calculated from the following equations [21]:

$$\Delta G^{\circ} = -RT \ln k_c \quad (3)$$

where R is the universal gas constant (8.314 J/Mol.K), T is the absolute temperature and K_c is the equilibrium constant.

K_c values were estimated as:

$$k_c = \frac{C_a}{C_b} \quad (4)$$

where C_a is the equilibrium concentration of dye on adsorbent (mg/l) and C_b is the equilibrium concentration of dye in the solution (mg/L).

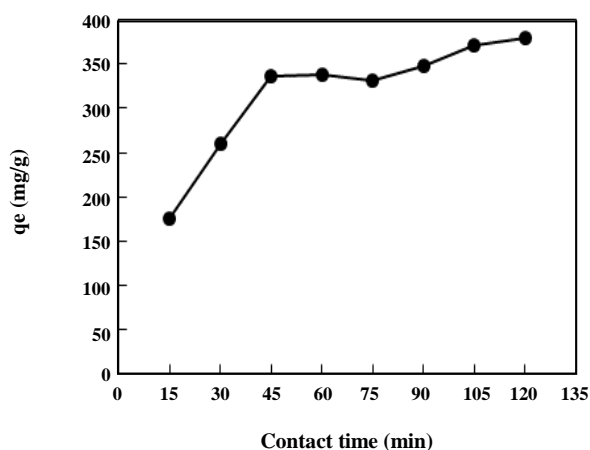


Fig. 3: Effect of adsorption time.

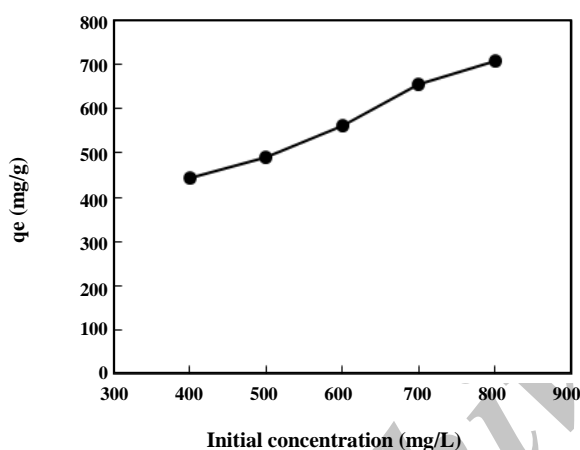


Fig. 4: Effect of initial dye concentration.

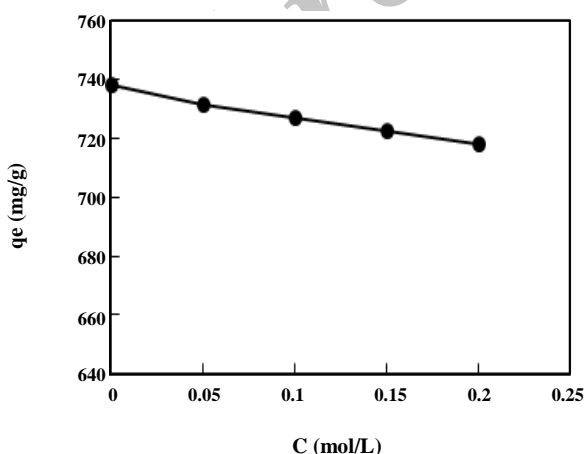


Fig. 5: Effect of ionic strength.

As shown in (Fig. 6.b), the ΔH° and ΔS° values were calculated from slope and intercept of the linear plot of $\ln K_c$ versus $1/T$.

$$\ln k_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

The corresponding values of thermodynamic parameters are presented in Table 1. The negative ΔG° values of $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ adsorption onto GO was due to the fact that the adsorption processes were spontaneous with a high preference of dye onto adsorbent. The positive value of ΔH° confirmed the endothermic character of adsorption system whereas the positive ΔS° values confirmed the increased randomness at the solid-solute interface during adsorption.

Adsorption isotherms

The equilibrium isotherms describe how the adsorbent interacts with the adsorbate. The correlation of experimental results to adsorption model can help to understand the mechanisms of adsorption and the heterogeneity of the adsorbent surface. Langmuir and Freundlich isotherm models were employed to describe the adsorption of $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ onto graphene oxide adsorbent. (Fig. 7).

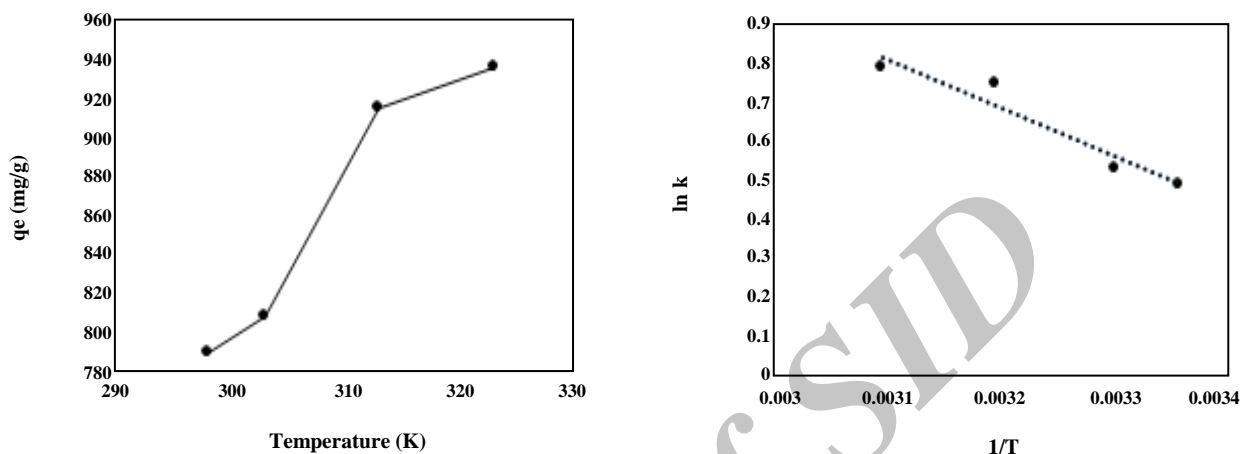
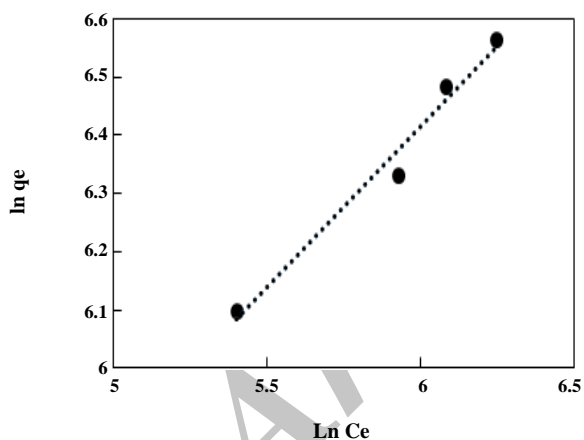
Langmuir's model [21] of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. The linear form of the Langmuir isotherm equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (6)$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L). q_m (mg/g) and b (L/mg) are the Langmuir constants related to maximum

Table 1: Thermodynamics quantities for adsorption of copper phthalocyanine on GO.

Temperature (K)	ΔH° (kJ/mol)	ΔS° (Kj/mol k)	ΔG° (Kj/mol)	Equilibrium constant
303	10.48	0.039	-1.33	1.69
313	10.48	0.039	-1.94	2.11
323	10.48	0.039	-2.11	2.2

**Fig. 6: (a) Effect of temperature; (b) $\ln K_1$ vs. $1/T$ plot.****Fig. 7: Linear form of Freundlich isotherm for GO/[Cu(tsPc)⁻⁴.4Na⁺] adsorption system.**

monolayer adsorption capacity and energy change in adsorption, respectively. Langmuir constants were calculated and recorded in Table 2.

The Freundlich model [23] is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and is not restricted to the formation of the monolayer.

The Freundlich model considers different affinities for the binding sites on the adsorbent surface with interactions between the adsorbed molecules. The linear form of the Freundlich isotherm equation is:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (7)$$

where K_f is the Freundlich constant ($\text{mg/g}(\text{mg/L})^n$) and the slope $1/n$ ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [24]. Freundlich constants were calculated and listed in Table 2.

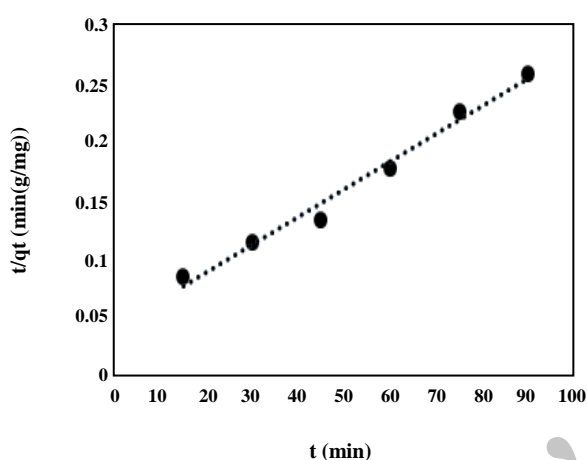
By comparing the results presented in Table 2 based on the correlation coefficients (R^2 value) it can be seen that the Freundlich isotherm is more suitable model for the adsorption of $[\text{Cu}(\text{tsPc})^{-4}.4\text{Na}^+]$ onto graphene oxide. Very high adsorption capacity (q_m) calculated from Langmuir isotherm shows the high tendency of (CuTSPc) to attach on the surface of graphene oxide. Since ionic strength did not have major effect on this adsorption system, this high adsorption capacity must be attributed to π - π stacking interactions between polycyclic aromatic structure of (CuTSPc) and unsaturated bonds on the surface of graphene oxide.

Table 2: Isotherm constants for adsorption of [Cu(tsPc)⁻⁴.4Na⁺] on GO.

isotherms	parameters	data
Langmuir	q _m	1250
	b	0.0023
	R ²	0.9366
Freundlich	K _f	22.096
	N	1.807
	R ²	0.9767

Table 3: Kinetic parameters for adsorption of [Cu(tsPc)⁻⁴.4Na⁺] on GO.

Kinetic models	parameters	data
Pseudo first order	q _e	382.56
	b	0.0377
	R ²	0.9706
Freundlich	q _e	416.66
	K ₂	0.00013
	R ²	0.9828

**Fig. 8: Pseudo second order kinetic model for GO/[Cu(tsPc)⁻⁴.4Na⁺] adsorption system.**

Adsorption kinetics

Adsorption kinetics are of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. In this study two kinetic models were employed to describe the adsorption of [Cu(tsPc)⁻⁴.4Na⁺] onto GO. (Fig. 8).

In 1898 Lagergren presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption based on the adsorption capacity (q_e). To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order [25]. In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in different fields. The linear form of pseudo-first order rate equation can be represented as following form [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g); k₁ is the rate constant of pseudo-first order adsorption (L/min).

In 1995 Ho & McKay presented a second order rate equation for adsorption of divalent metal ions onto peat. Similar to Lagergren's equation, this equation has been called pseudo-second-order rate equation.

Linear form of this equation is [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

Where the equilibrium adsorption capacity q_e, and the pseudo-second order constants k₂ (g/(mg min)) can be determined experimentally from the slope and intercept of the plot t/q_t versus t.

Regarding to Table 3 it is clear that the pseudo-second-order kinetic model gives a better correlation for the adsorption of [Cu(tsPc)⁻⁴.4Na⁺] onto graphene oxide compared to the pseudo-first-order model.

CONCLUSIONS

The present study shows that graphene oxide has a high affinity to [Cu(tsPc)⁻⁴.4Na⁺] as an anionic dye. The equilibrium time was independent of initial dye concentration. The adsorption kinetic studies showed that the adsorption process followed pseudo-second order model, indicating that the rate-limiting step may be chemisorption and that the rate equation follows second-order kinetics. Freundlich model was successfully applied to show that the adsorption of [Cu(tsPc)⁻⁴.4Na⁺] onto graphene oxide is not restricted

to formation of the monolayer. The thermodynamic parameters indicated spontaneous and endothermic process and rise in temperature favored the adsorption.

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