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Synthesis and Characterization of Graphene Oxide for Efficient Adsorptive Removal of Hymexazol Pesticide from Aqueous Solutions: Thermodynamic, Kinetic, and Isotherm Studies

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ABSTRACT: ***Background:*** *Nanomaterials play a significant role in the field of water treatment due to their environment-friendly and appealing physical and chemical characteristics.* ***Objective:*** *The purpose of this research is to evaluate whether graphene oxide adsorbents can effectively remove hymexazol pesticide from an aqueous solution.* ***Methods:*** *Graphene oxide (GO) was prepared by the modified Hummer method, and it was characterized by a number characterization techniques, including XRD, Raman spectroscopy, FE-SEM, TEM, and EDX. Furthermore, the performances of the GO adsorbents for the removal of hymexazol from aqueous solution were investigated. The effect of contact time, GO dosage, initial hymexazol concentration, and temperature was carefully studied.* ***Results:*** *The kinetic experimental data were best described by the pseudo-second-order kinetic model. The equilibrium data were well fitted by the Freundlich and Langmuir isotherm models. The kinetic experimental data were best described by the pseudo-second-order kinetic model. And through the thermodynamic studies, it was found that the adsorption process of hymexazol pesticide is endothermic and spontaneous, in addition to the occurrence of adsorption and absorption together.* ***Conclusions:*** *The findings of the adsorption process demonstrated that graphene oxide is an extremely efficient adsorbent material for pesticide adsorption, owing to its large surface area and the presence of oxygen-rich groups on its surface.*

KEYWORDS: *Adsorption; Graphene Oxide; Hymexazol; Modified Hummer Method; Nanomaterial*

INTRODUCTION

Nanotechnology is an important development in contemporary science, which makes it possible to manufacture materials with unique structure, content, and size [1]–[4]. Nanotechnology-based methods have produced efficient ways and materials for the solution of many difficult problems, that prior and traditional techniques were unable to handle [5]. Nanotechnology has been applied in a variety of scientific and technological applications [6], including food industry [7], industrial processes [8], medical field [9], and environmental applications [10]. Nanomaterials also plays a significant role in the field of water treatment [11], due to the environment-friendly, appealing physical and chemical characteristics, such as increased material durability against mechanical stress or weathering, surface structure, and significant absorption, both in terms of adsorption capacity [12], [13]. A derivative of graphene, called graphene oxide (GO), has a special two-dimensional structure with -bonds connecting carbon atoms with Sp2-hybridization to form a honeycomb-lattice [14]–[16]. Functional groups including carbonyl, carboxyl, hydroxyl, and epoxy residues are abundant on its surface [17], [18]. The chemical characteristics of GO are substantially more active compared to graphene because of the existence of these oxygen-containing groups, which offer many locations for chemical reactions and ion/molecular interactions [19], [20].

GO has special properties such as high hydrophilic nature, large surface area, atomic thickness, high strength, exciting durability, and reactive sites for chemical reactions [18], [21], [22],which have generated significant interest in different science and technology fields [23]. Due to its exceptional physicochemical features, unique surface structures, and strong affinity, graphene oxide has received extensive research as a novel adsorbent [24], [25]. GO is extremely effective in adsorbing both organic and inorganic impurities from drinking water [26]. By means of coordination π–π interactions, electrostatic interactions, H-bonding, hydrophobic interactions, and H-bonding. The oxygen-containing groups enable the binding of positive-charge-organic-molecules and metal-ions [16], [27], [28].

Clean water is a vital component of ecosystems and is critical to the survival of Earth's life. It's common knowledge that having access to clean drinking water is essential for maintaining one's health and is also a fundamental human right [29], [30].

Water pollution from pesticide residue has been growing as agricultural needs for pesticide use have expanded, posing a huge hazard to the environment [31], [32].

Pesticides are among the most harmful organic pollutants, causing major health concerns such as cancer, endocrine dysfunction, and immunological dysregulation when present in water [33]–[35]. One of the pesticides that contaminates the environment is hymexazol [36], which has been classified as a hazardous substance for humans by the European Food Safety Authority (EFSA). According to research, the liver is the major target organ upon exposure to the hymexazol pesticide. Hymexazol pesticides are particularly toxic to fish embryos, resulting in swing abnormalities, growth retardation, and heart edema [37], [38].

The aim of this research is to prepare graphene oxide by the modified Hummers method and use it as an adsorbent to remove hymexazol pesticide from aqueous solutions. The structure and morphology of the prepared graphene oxide were studied. And study the thermodynamics, isotherms, and kinetics of the adsorption process.

MATERIALS AND METHODS

Graphite powder (99.9%), Sulfuric acid (98%), hydrochloric acid, potassium permanganate (99.5%), distilled water, sodium nitrate (99%), hydrogen peroxide (30%), hymexazol (36%) SL, deionized water.

Synthesis of Graphene Oxide

According to the modified Hummers method, graphite (2 g) and $NaNO_3$ (1 g) were mixed with 100 ml of H2SO4 (98%). Und kept stirring with temperature control (≈5 °C) for 30 min. Then, 5 g of $KMnO_4$ was gradually added to the mixture and kept stirring for 5 hours. After that, 1 L of distilled water was added to the mixture. Then 30% H_2O_2 is added in a volume of 20 ml to the mixture for stopping the reaction. Following that, the product precipitate underwent centrifugation to be separated, and it was repeatedly washed with de-ionized water and 12% HCl solution. At room temperature, the dark brown product was allowed to dry overnight to produce GO [39].

Adsorption Experiment

Adsorption experiments were conducted using the hymexazol pesticide at concentrations ranging from 10 to 50 ppm. With the addition of varying amounts of the GO (0.01-0.15 g) to ten milliliters of the hymexazol pesticide solution at a particular concentration. After that, the mixture was agitated in an orbital shaker with continuous stirring at 185 rpm to complete the adsorption process for a specific time. After that, the GO was separated from the solution by centrifugation for 15 min. A UV-Vis spectrophotometer was used to determine the residual pesticide concentration at 238 nm. The amount of the adsorbed pesticide (Qe) and the removal efficiency (R%) were estimated using the equations below [39]–[41]:

$$Q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

$$R\% = \frac{C_0 - C_0}{C_0} \times 100\% \tag{2}$$

Where is Qe is equilibrium capacity (mg/g), Co and Ce are initial and equilibrium pesticide concentration (ppm), respectively. V is volume of pesticide (l), and M is mass of GO (g).

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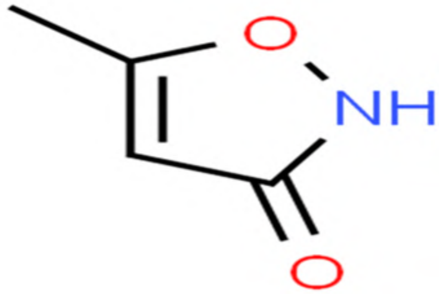

Figure 1. Chemical structure of hymexazol [42]

RESULTS AND DISCUSSION

Characterization

The crystallite size and crystal phases of synthesized GO were investigated using the XRD technique with Cu Ka radiations ($\lambda = 1.5406$ nm) in 2θ. Figure 2, shows the XRD patterns of GO in the 10-80° range. The diffraction peaks of GO were detected around $2\theta = 26^{o}$ corresponding to (002) and $2\theta = 42°$ corresponding to (100) were referred to the carbon structure in graphite. The broad peak corresponding to the (002) at $2\theta = 26°$ indicating the inclusion of oxygen functional groups during the oxidation of graphite [43].

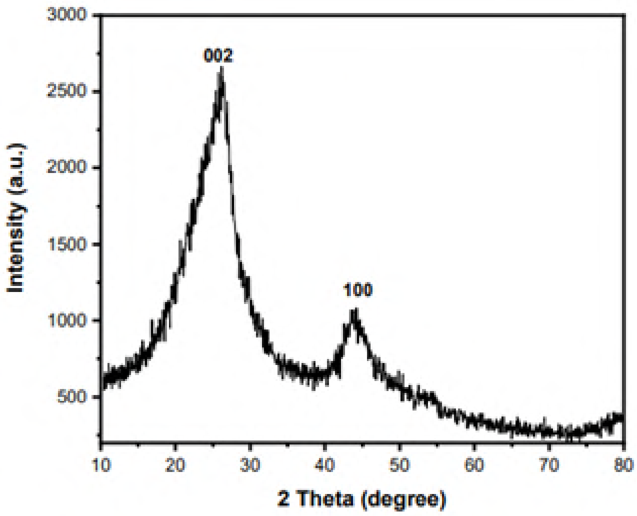

Figure 2. XRD of GO synthesis using the hummer method

Raman spectroscopy is powerful and non-destructive analytical approach. Utilized to obtain information about carbon-based material's structure and properties. [44], [45]. The G and D bands are the most commonly used characteristics of the spectrum to track changes throughout different treatments [46]. Typical Figure 3, depicts the GO Raman spectra. peaks near (1350 and 1590 cm^{-1}) could be seen in the produced GO sheets' Raman spectra. In the case of GO, the D is obtained at 1350 cm^{-1} and G peaks is at obtained 1590 cm^{-1}. The stretching of the C-C bond is attributed to the G peak, The presence of functional groups containing oxygen on graphene sheets is associated to D-peak [47], [48]. The 2D bands, which have two peaks at (2600 cm^{-1} and 2950 cm^{-1}).

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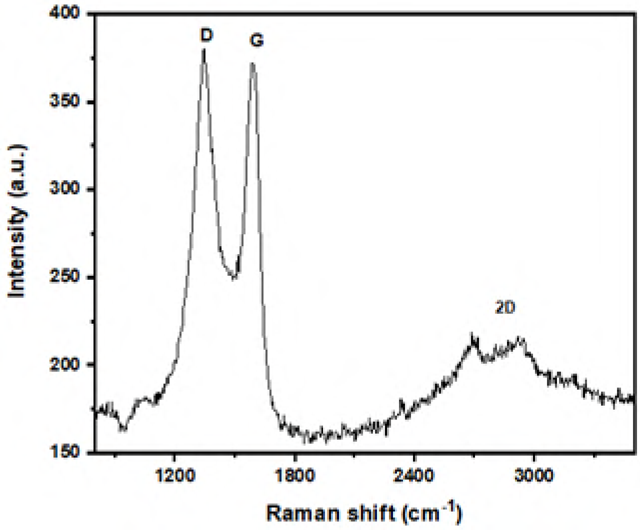

Figure 3. Raman spectra of GO

The morphology of the produced GO as determined by FE-SEM as shown in Figure 4. Where the 2D structure of GO with several thin layers was observe. This layer developed in wrinkled forms, one on top of another, this is due to graphite exfoliation that produces graphene oxide, which causes restacking and exfoliation [49].

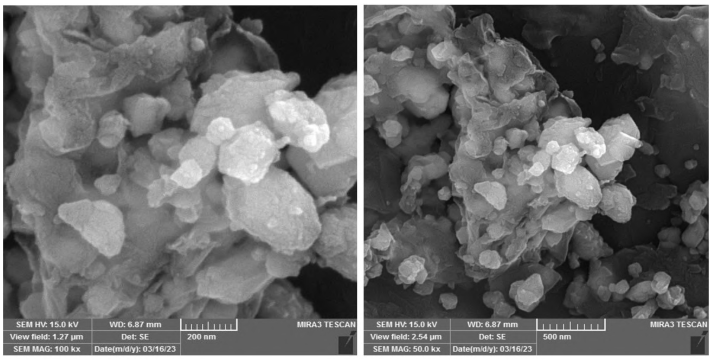

Figure 4. FESEM image of GO

The TEM image of synthesized GO shows in Figure 5, that the higher degrees of clarity signify significantly thinner films of a few layers of GO formed through stocking exfoliation. Some wrinkling of the sheets can also be observed; this is due to the presence of oxygen-rich functional groups associated with graphene sheets [50].

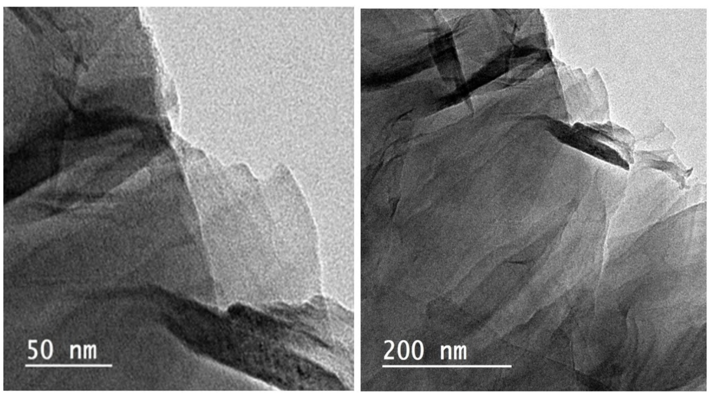

Figure 5. TEM image of GO

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Through HRTEM analysis, direct information can be obtained about the atomic level of graphene oxide [51]. Figure 6, shows the finger print of prepared GO (d-spacing 0.24 nm), which belongs to the graphitic structure [52].

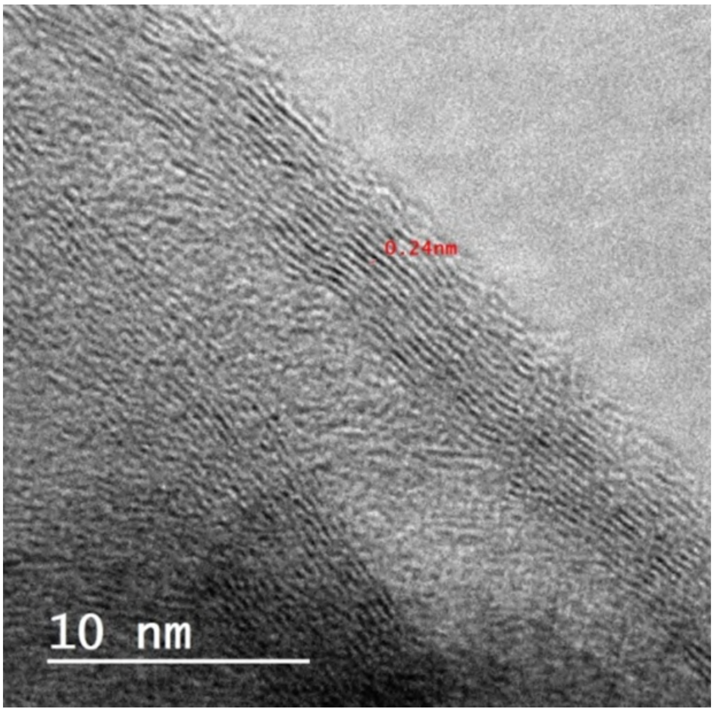

Figure 6. HRTEM of GO

EDX analysis confirmed the high purity of GO. Through Figure 7, prepared GO consists of 57.7% Carbon and 43.3% Oxygen.

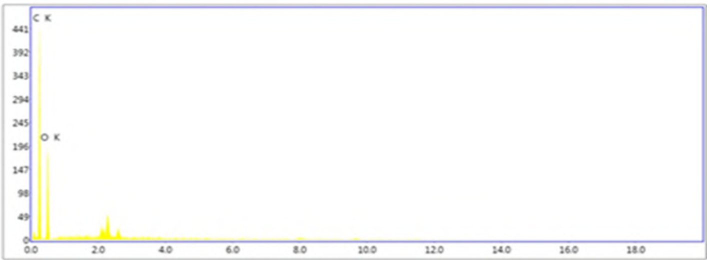

Figure 7. EDX image of GO synthesis using hummer method

Figure 8, shows the regular distribution of the O and C atoms on the GO surface, this indicating that the atoms adopt multiple places in the sample, giving a wide area for diffusion, which is one of the characteristics of nanomaterials where they are the smallest sizes and a large surface area.

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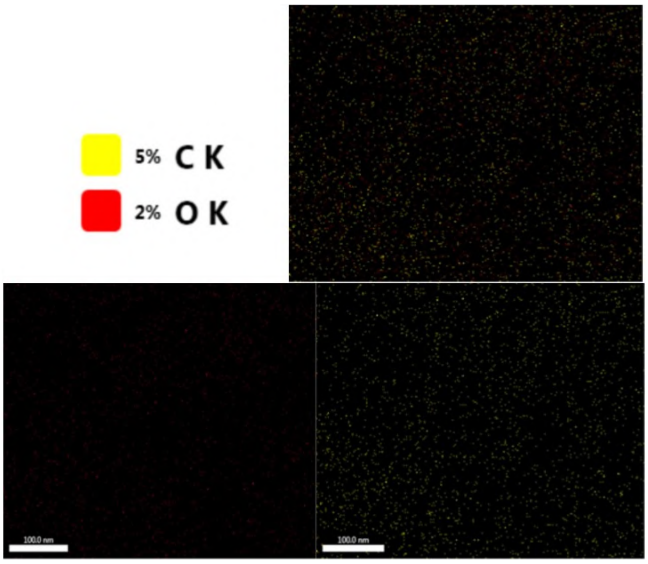

Figure 8. X-ray mapping of GO nano-sheet synthesis using the hummer method

Adsorption study

Effect of Contact Time

The effect of connect time was studied by adding 0.01 g of GO to 10 mL of hymexazol solution (50 ppm) at 25 °C with a stirring speed of 185 rpm at various intervals of time in the adsorption of hymexazol pesticide. It was observed that the removal efficiency increased directly with the increase in contact time, reaching equilibrium at 60 min. After that, the rate of the adsorption process became constant, in order to saturate the active sites with hymexazol molecules, and only a few of them are still active, so it takes a longer time to perform the adsorption process [53].

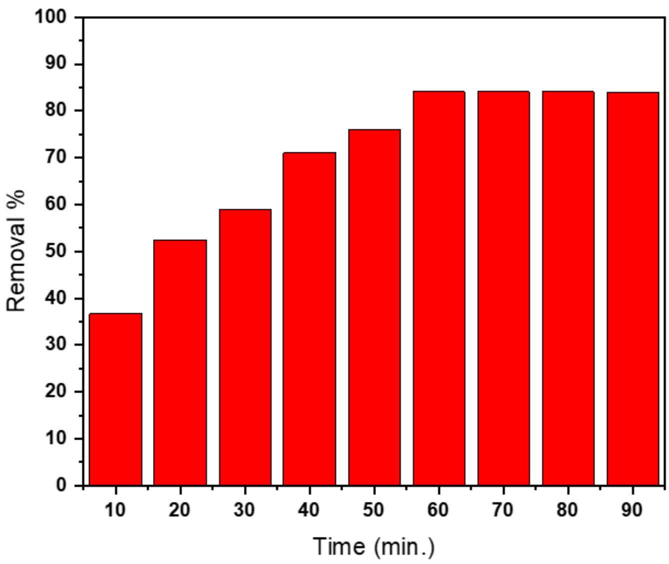

Figure 9. Effect of contact time on adsorption of hymexazol pesticide

Effect of GO Dosage

The effect of GO dosage on the pesticide adsorption was investigated by adding different amounts of GO within the range (0.01-0.15 g) to 10 ml of hymexazol pesticide solution (50 ppm). Figure 10, shows that the removal efficiency of hymexazol pesticide increased with increasing dose of GO, due

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to the increase of the active sites on the GO surface [54], as a result, more hymexazol molecules were removed from the solution until total saturation was achieved.

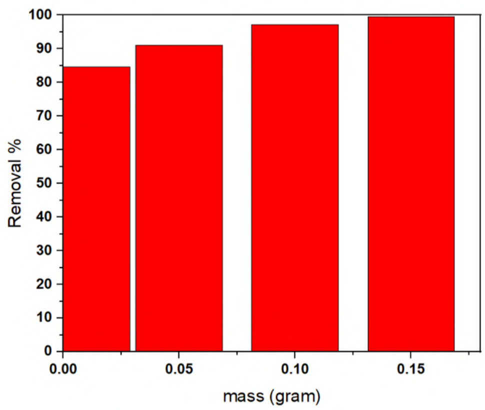

Figure 10. Effect of GO dose on adsorption of hymexazol pesticide

Effect of Temperature and Thermodynamic Parameter Calculation

These experiments were conducted at five specific temperatures, from 288 to 328 K, to investigate the temperature effect on the effectiveness of GO for the adsorption of hymexazol pesticide.

An increase in temperature leads to an increase in adsorption efficiency. This is due to an increase in both the surface energy and molecular diffusion of hymexazol pesticides on the surface of GO with the increase in adsorption temperature Adsorption efficiency increases with temperature. This is due to an increase in both the surface energy and molecular diffusion of pesticides on the surface of nanomaterials, enhanced strong binding linked the hymexazol molecules and surface of GO.

The thermodynamic parameters, including entropy change (ΔS), enthalpy change (ΔH), and Gibbs energy change (ΔG), reveal specific information about the mechanism and nature of the adsorption process. The following equations is used to determine the thermodynamic parameters [55], [56]:

$$\ln(K_e) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

$$K_e = \frac{Q_e}{C_e} \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

where Ke is an equilibrium constant, R is a gas constant (8.314 J/mole.K), and T is the temperature in Kelvin. From the slope and interception of the plots of van't Hoff, ΔH and ΔS were identified as shown in Figures 11. The S value was found to be 87.47 (J/mole.K) from the intercept, which suggests that the surface of the adsorbent becomes more random and disordered. The corresponding ΔH from the slope was 21.87 (kJ/mole), which indicated the process was endothermic. And G was determined to be -4.199 (KJ/mole), which means spontaneous adsorption.

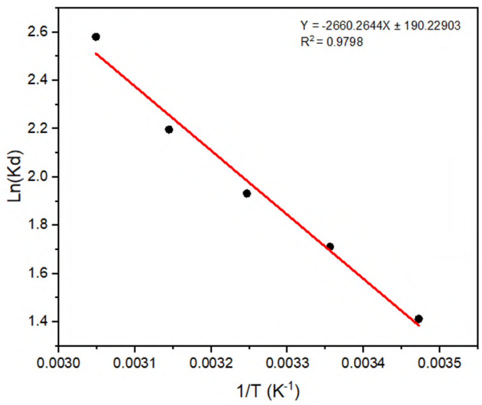

Figure 11. Van't Hoff' plot relation between $\ln(K_e)$ and $\frac{(1)}{T}$ for hymexazol adsorption

Adsorption Kinetics

The study of kinetic adsorption is very important to know the mechanism and response rate of the adsorption process [57].

The present study used two kinetic models, pseudo-first-order and pseudo-second-order models, to investigate the kinetics and controlling mechanisms of the adsorption hymexazol pesticide process. The linearized form of the pseudo-first-order model equation is generally described as [58]:

$$\ln(q_e - qt) = \ln(q_e) - k_1 t \tag{6}$$

The pseudo-second-order model equation is given as [59]:

$$\frac{1}{qt} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \tag{7}$$

Where qt and qe (mg/g) amount of pesticide adsorbed at time t (min) and equilibrium (mg/g), respectively. K1 (1/min) is rate constants of pseudo-first order, and K2 (g/mg min) is rate constants of the pseudo second-order.

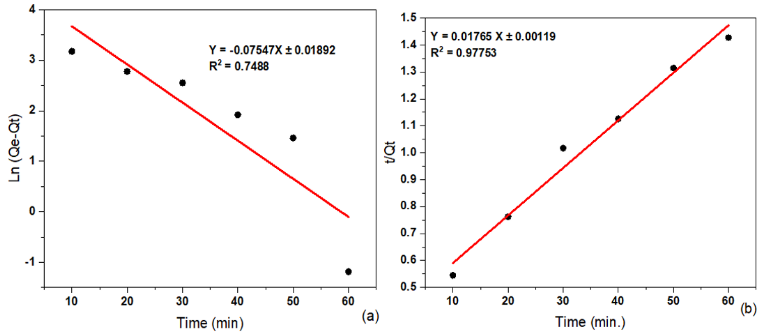

Figure 12. Kinetic of adsorption Hymexazol pesticide: (a) pseudo-first-order and (b) pseudo-second-order

Table 1. Kinetic parameters for adsorption of hymexazol pesticide

pseudo first order	**K1 (min^{-1})**	**R^2**
	0.0013	0.7488
pseudo second order	**K2 (g.mg/min)**	**R^2**
	0.0008	0.9775

A pseudo-second-order model with a high correlation coefficient (R2 > 0.9775) can accurately describe the kinetic information; this also suggests that the adsorption mechanism was improved via chemisorption, which involves the share of electrons that take place between the adsorbent surface and the adsorbate molecular [60].

Adsorption isotherms

Adsorption data should be fit with isothermal adsorption in order to comprehend the relationship between the surface of GO and the hymexazol. In this study, both the Freundlich and Langmuir isotherm models were considered. The following equation represents to the Freundlich isotherm model [61]:

$$\log_n(Q_e) = \log_n(kf) + \frac{1}{n}\log_n(Ce) \tag{8}$$

Adsorption capacity (Kf) and adsorption intensity (n), which refer to the Freundlich constants. Kf can be found from the slope, while n is obtained from the intercept.

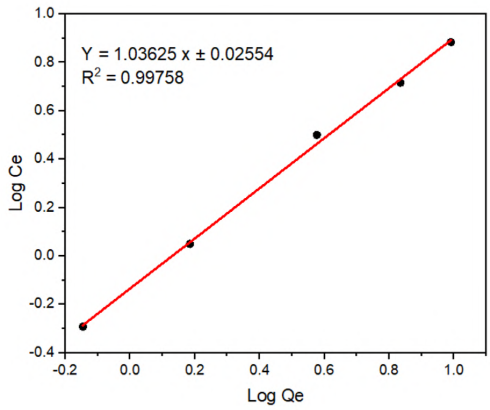

Figure 13. Freundlich isotherm for adsorption of hymexazol pesticide

The value of 1/n was determined to be 0.519, and these findings demonstrate its favorable physical adsorption [62]. Langmuir isotherm model is given by equation (9) [63]:

$$\frac{e}{q_e} = \frac{1}{(q_{max} \cdot K)} + \frac{c_e}{q_{max}} \tag{9}$$

Which q max is maximum amount of hymexazol adsorbed per gram of GO, and KL is Langmuir constant.

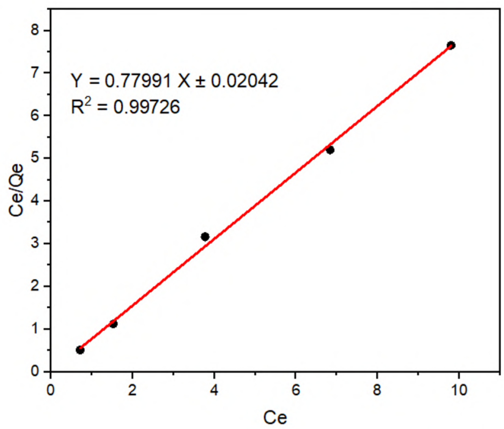

Figure 14. Langmuir isotherm for adsorption of hymexazol pesticide

Based on the correlation coefficient (R2) values, both the Freundlich and Langmuir models very closely fit the adsorption process.

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A separation factor (RL) was used to determine the suitability of an adsorption process. RL is given by the following equation [64]:

$$RL = \frac{1}{1 + KL \cdot Ci} \tag{10}$$

The RL value was determined to be 0.0194, which indicates the adsorption process is favorable [65].

CONCLUSION

High-quality GO was prepared by a modified Hummer method according to the XRD, Raman spectroscopy, FESEM, TEM, and EDX characterizations. The prepared GO was used to remove the hymexazol pesticide from aqueous solutions. The findings of the adsorption process demonstrated that graphene oxide is an extremely efficient adsorbent material for pesticide adsorption, owing to its large surface area and the presence of oxygen-rich groups on its surface. The equilibrium data were well fitted by the Freundlich and Langmuir isotherm models. The calculations of the thermodynamic parameters gave the adsorption values for ΔS, ΔH, and ΔG equal to 21.87 (kJ/mole), 87.47 (J/mole), and -4.199 (KJ/mole), respectively. These results demonstrate that the adsorption was endothermic and spontaneous.

SUPPLEMENTARY MATERIAL

None.

AUTHOR CONTRIBUTIONS

Ahmed Mahdi Rheima suggested the research idea, Ahmad Hussain Ismail performed the theoretical section, and Fatima Mohammed Abdullah organized all the results and data and wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

FUNDING

None.

DATA AVAILABILITY STATEMENT

None.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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