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Effective removal of Hymexazol pesticide from polluted water using cadmium oxide nanoparticles prepared by photolysis methods: Thermodynamic, kinetic, and isothermal studies

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Abstract

The problem of water pollution with pesticides is one of the most dangerous types of pollution, as it is considered one of the most important causes of cancer for humans, as well as the destruction of the aquatic environment. Currently, several techniques have been used to solve this problem, the most prominent of which is the adsorption technique. The purpose of this study is to investigate the removal of hymexazol pesticide from an aqueous solution by using a cadmium oxide nanopartical adsorbent. CdO NPs were prepared by the photolysis method, and they were characterized by several characterization techniques, such as XRD, TEM, and FE-SEM. Batch adsorption experiments were performed using a variety of factors, such as contact time, adsorbent dose, initial pesticide concentration, and temperature. The results showed that the removal efficiency of hymexazol pesticide on CdO NPs was the highest at a contact time of 50 minutes. The equilibrium data were well fitted with Freundlich mode. The kinetic investigations reveal that the pseudo-second-order model can describe hymexazol pesticide adsorption processes. According to the thermodynamic study, hymexazol pesticide adsorption is a physisorption-endothermic and spontaneous process.

Keywords: Adsorption, Cadmium Oxide nanopartical, Hymexazol, Pesticide, Nanotechnology, Water contamination

Introduction

The availability of clean water is one of the most indispensable elements of basic need for the survival of humankind and all ecosystems (Mondol, 2020) (Kumar, 2023). However, due to population growth and the wide variety of agricultural, domestic, and industrial wastes that have badly contaminated both surface and groundwater via the sewer system, water quality and adequacy have become serious concerns (Chowdhary, 2020) (Aguilar-Pérez, 2022) (Rai, 2023).

Water contamination is regarded as one of the most serious problems in the globe (Raghu, 2021). The water contaminants are generally classified as microorganisms, organic chemicals, and inorganic toxic elements (Shahi Khalaf Ansar, 2022). Pesticides are one of the most persistent organic pollutants (Trellu, 2021). They are characterized by being highly soluble in water (Dugan, 2023) and non-selective contact compounds that can cause serious environmental problems (Nguyen, 2023). They are highly harmful, even in low concentrations (Boher, 2023). Hymexazol is one of the pesticides that cause environmental pollution (Yousfi, 2022). The European Food Safety Authority (EFSA) has identified hymexazol as a toxic agent for humans. According to research, when exposed to the hymexazol pesticide, the liver is the primary target organ. Hymexazol pesticide is considered extremely harmful to embryonic fish, causing growth retardation, heart edema, and swing abnormalities (Hassanen, 2022) (Hassan, 2023).

Recently Nanotechnology plays an important role in current environmental practices for remediation of contaminants (Abla, 2023), which is focused on the development and fabrication of novel nanomaterials with well-defined and controle morphologies of proper size and shape for efficient wastewater treatment to replace the scarce and expensive traditinal material (Adegoke, 2023). Nanomaterials also have many excellent chemical and physical properties, including their small size, large surface area, strong adsorption capacity, high chemical reactivity, mechanical characteristics, low power consumption, and cost-effectiveness (Nagrath, 2023) (Kishore, 2023), which gives it the potential to eliminate different toxins, for instance, organic pollutants, pathogens, heavy metals, and inorganic anions (Mondal, 2023) (Abdullah, 2022). Among nanomaterials, CdO is classified as an n-type semiconductor material having a wide energy band gap, ionic nature, and low electrical resistivity (Korotcenkov, 2023). And shows applications in in environmental applications, where it is used as an adsorbent to remove pollutants from the water environment (Bukhari, 2023)**.**

The aim of this work was to synthesize Cadmium oxide nanoparticals by the photo-irradiation method and use it as a nanoadsorbent for the removal of hymexazol pesticide from aqueous solutions. The structure, morphology, and properties of the synthesized SrO NPs were investigated. Also the thermodynamics, isotherms, and kinetics of the adsorption process were evaluated.

Martial and methods

Cadmium nitrate [$Cd(NO_3)_2$], Sodium hydroxide (NaOH), urea ($(NH_2)_2CO$), and Hymexazol pesticide were supplement from sigma Aldrich without any purification. Cadmium Oxide Nanoparticles (CdO NPs) were synthesized by the photo-irradiation method. The photocell consists of a reactor, a pyrex container containing a saline solution as a source for the nanomaterials to be prepared, a mercury lamp (125 watts) as a source of ultraviolet radiation with a maximum wavelength of 365 nm, This lamp is protected by a tube of quartz, and the tube is immersed in the saline solution. An ice bath is used to avoid the high temperature caused by ultraviolet radiation, as shown in Figure 1.

Accordingly, 100 ml of urea (0.02 mole) was added slowly (one drop per second) to 100 ml of strontium nitrate (0.01 mole) with sonication for 20 min using an ultrasonic device. Then, the solution was irradiated for 30 minutes by a photocell. With cooling under 5°C. After that, 1 M of 20 ml NaOH was added to the solution. A white precipitate appears due to Cd(OH)2, which is separated by a centrifugation process and then washed with deionized water many times. For one hour at 120°C, the precipitate was dried and calcined at 450°C for 3 hours. A white precipitate of CdO NPs was obtained.

Figure 1. The Photo-cell (Kamil, 2021)

Adsorption Experiments

Hymexazol pesticide ($C_4H_5NO_2$) was used to conduct adsorption experiments at concentrations (10, 20, 30, 40, and 50 ppm). Unter the addition of different quantities of the adsorbent (0.01, 0.05, 0.1 and 0.15 g) to 10 ml of the solution containing a certain concentration of the pesticide. After that, the volumetric flask containing the mixture was placed in a water bath with continuous stirring at 185 rpm. With time periods ranging from 10 to 90 minutes, and the equilibrium time was found at 50 minutes. After that, the solution was centrifuged for 15 minutes to separate the CdO NPs from it. Then, the absorbance of the pesticide solution was measured after adsorption using UV/Vis spectroscopy, at a wavelength of 238 nm.

The equations shown below were used to calculate the amount of Hymexazol pesticide adsorbed (Qe) in (mg/g), and the removal percentage (R%) (Balci, 2022) (Chen, 2023):

$$Qe = \frac{(C_0 - Ce)\,V}{M} \qquad (1)$$

$$R\% = \frac{(C_0 - Ce)}{C_0} \times 100\ \% \qquad (2)$$

where C_0 and C_e is initial and equilibrium Hymexazol pesticide concentrations at ppm, V is the solution's volume (L), and M is mass of adsorbent.

Characterization of CdO NPs

XRD of CdO NPs

The XRD of the CdO NPs observed peaks at 25.398°, 30.518°, 33.012°, 36.617°, 43.991°, 46.817°, 50.103°, 57.572°, 65.628° and 69.259° which can be well indexed to the (220), (311), (111), (331), (422), (511), (440), (311) and (222) planes of cubic CdO NPs (JCPDS card no. 73-2245) and (JCPDS card no. 01-104). The average crystal size is equal to 26.38 nm.

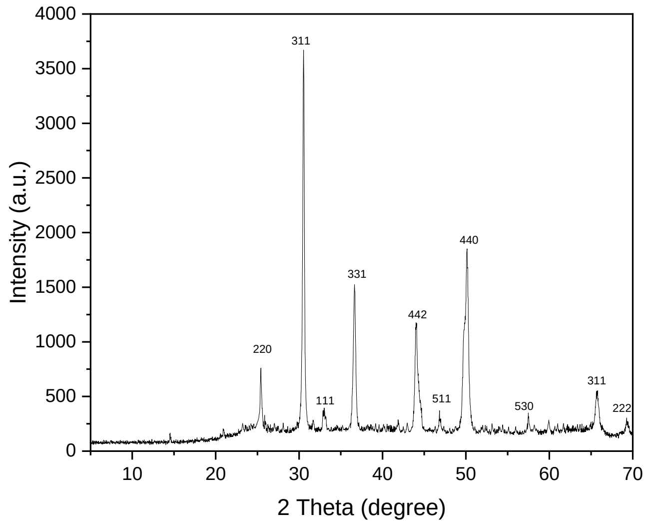

Figure 2. XRD of CdO NPs

Transmission electron microscopy

TEM images revealed that the synthesized CdO NPs particles appear to be of spherical shape with a non-uniform distribution; the average particle size was found to be 12 nm. The spherical-shaped particles, which have a larger surface area than other geometric shapes, higher surface energy, and larger surface area of nanoparticals, may be attributed to the agglomeration of CdO NPs (Shimi, 2022).

Figure 3. Tem image of CdO NPs

Field emission scanning electron microscopy (FESEM)

FESEM was used to understand the surface morphology and shape of CdO NPs. In figure 4, the surface of CdO NPs is smooth with good crystallinity. We note that the samples contain a high porosity through the measurement images, which indicates amorphous ratios in the samples.

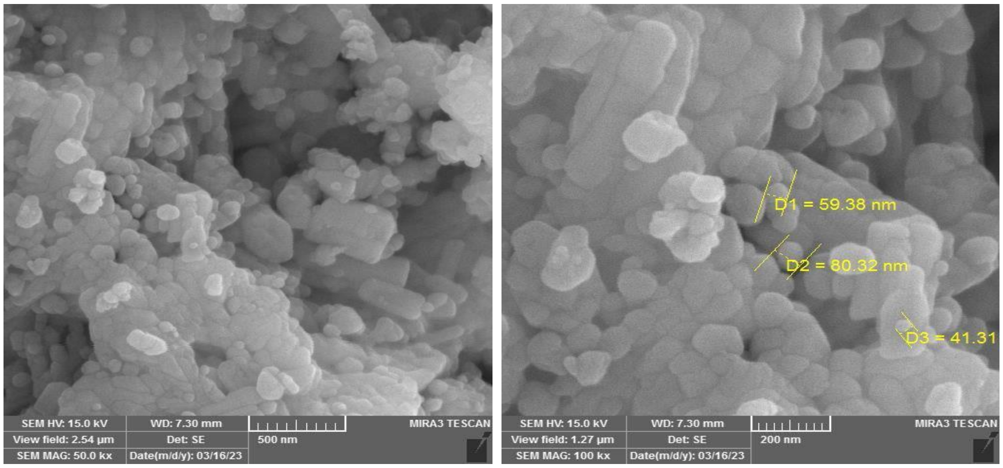

Figure 4. FE-SEM analysis of CdO NPs

Adsorption

10 mL of hymexazol pesticide solutions (50 ppm) was shaken together with 0.01 g of nanocomposite at different time intervals ranging from 10 to 90 min, and the results are presented in Figure (5). The result obtained shows that the adsorption of pesticide generally increases with time, until it reaches a point where the adsorption behavior attains equilibrium status at 50 min. The fact that the overall number of active sites on the nanocomposite surface is initially fairly high and permits quick adsorption suggests this characteristic. However, the active sites become saturated with time, and only a small number remain active; thus, the adsorption process takes longer to complete.

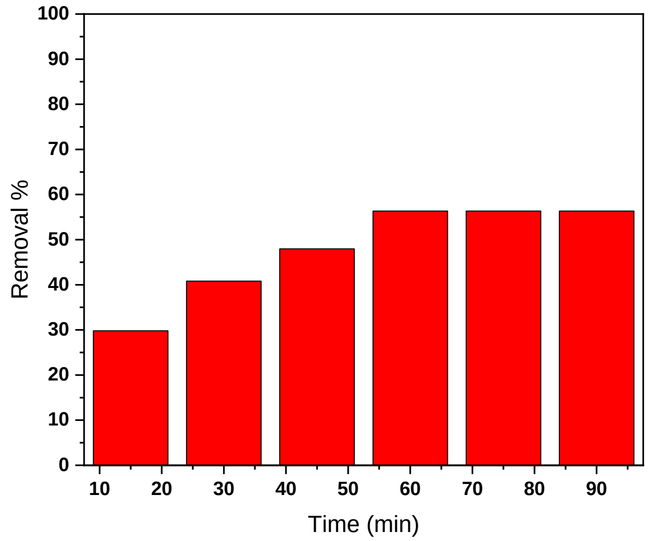

Figure 5. Effect of conect time on hymexazol adsorption

Dosage of CdO NPs effect

The influence of CdO NPs dosage (0.01–0.1 g) on the adsorption of Hymexazol (50 ppm) was investicated at 298K. After 50 minutes of agitating the mixture, the remaining pesticide concentration was determined. The results found that as adsorbent dosage increased, the removal efficiency of hymexazol increased. Which due to increased in the total surface area and more adsorption sites are available offered at the higher dosage (Batool, 2023).

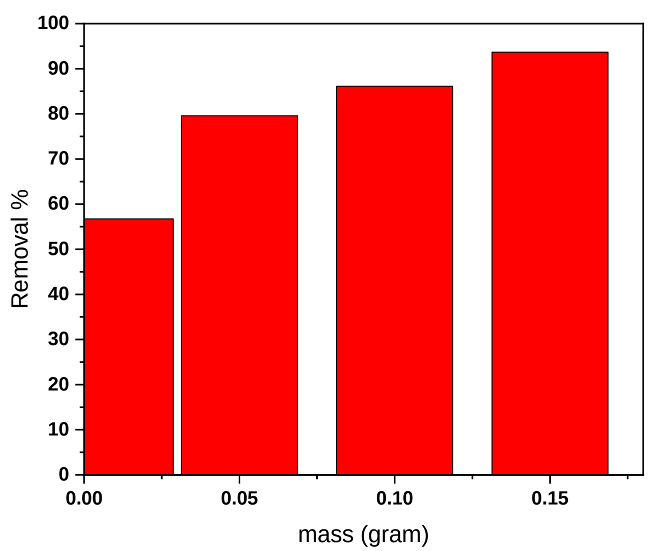

Figure 6. Effect of CdO NPs dose on hymexazol adsorption

Initial concentration effect

To design any adsorption system, pollutant concentration is considered an important parameter. During adsorption process the influence of hymexazol concentration was checked and it was observed that when the initial of pesticide concentration increased from (10 ppm) to (50 ppm) the removal percentage decreased from 91.38 % to 56.73%. In general, as the initial concentration of a pesticide in a solution increases, the active site of on the adsorbent's surface becomes saturated, resulting in decreased removal efficacy (Ali, 2022).

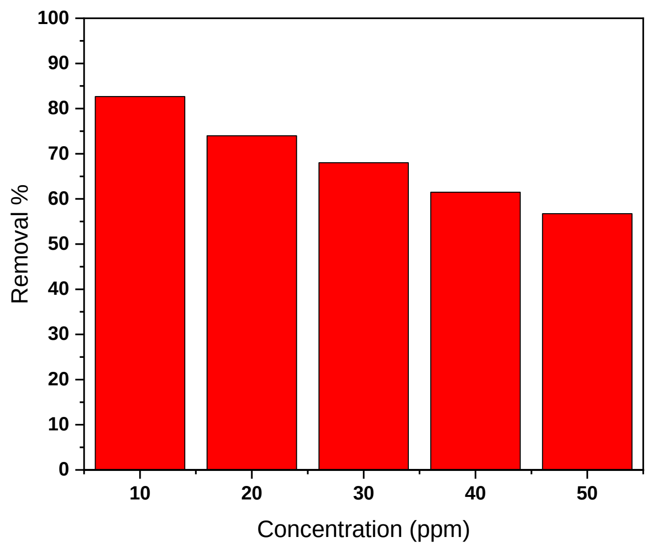

Figure 7. Effect of hymexazol concentration

Temperature effect and thermodynamic parameter calculation

At specific temperatures of (15, 25, 35, 45, and 55°C), the temperature effect on the pesticide adsorption on CdO NPs surface was studied. Increasing the temperatures lead to an increase in hymexazol pesticide adsorption efficiency. Where the increase in temperature causes to increases the rate of diffusion of hymexazol molecules inside the a surface of CdO NPs, reinforced the strong bond that links the hymexazol molecular and surface of CdO NPs.

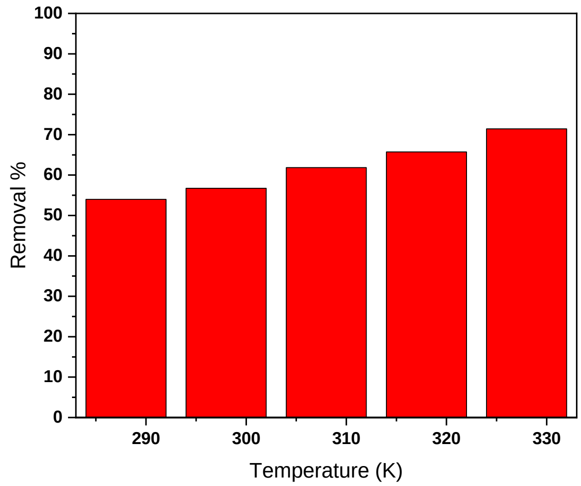

Figure 8. Effect of temperature on hymexazol adsorption

Thermodynamic parameters provide specific details on changes in the inherent energy produced by adsorption. In this study, to anticipate the adsorption mechanism, the enthalpy (ΔH°), entropy (ΔS°), and free energy (ΔG°) of adsorption were evaluated using equations (Qi, 2021) (Aragaw, 2022):

$$\ln(Ke) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4)$$

$$Ke = \frac{Qe}{Ce} \qquad (5)$$

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

where Ke is equilibrium constant, R is gas constant (8.314 J/mol K), and T is the temperature(K).

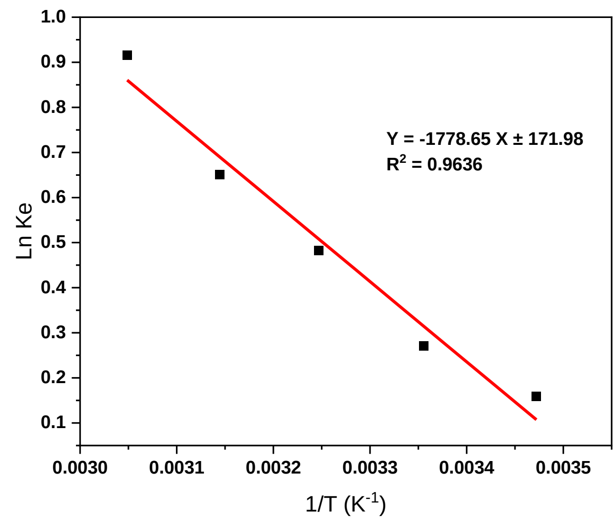

Figure (9). (van't Hoff) plot of adsorption of hymexazol pesticide on CdO NPs at different temperatures

From van't Hoff curve between Ln Kd and 1/T. ΔH and ΔS were specified as shown in Fig.10. The (ΔH°) was 14.97 (kJ/mole) by slope deterrence, It indicated an endothermic process, (ΔS°) value was 52.24 (J/mol K) from intercept, which indicates the adsorbent surface's increasing randomness and disorder after adsorption. And (ΔG°) value equal to -0.779 (KJ/mole), that means spontaneous and practicable adsorption process.

Adsorption Kinetics

Kinetic study was used to investigate adsorption mechanisms based on data from experiments and the rate priming stage (Zair, 2022). Pesticide adsorption on the CdO NPs surface was investigated by using, two kinetic models: pseudo-first order (PFOM) and pseudo-second order (PSOM) above as follows:

The pseudo-first-order equation (Ahadi, 2022):

$$\ln(qe - qt) = \ln(qe) - k1t \qquad (7)$$

The pseudo-second-order equation (Alhares, 2023):

$$\frac{1}{qt} = \frac{1}{K2\,qe} + \frac{t}{qe} \qquad (8)$$

Where qe and qt (mg/g) is the adsorption capacity at equilibrium and time, K1 (1/min) is the first-order adsorption rate constants, and K2 (g/mg min) is the second-order rate constant.

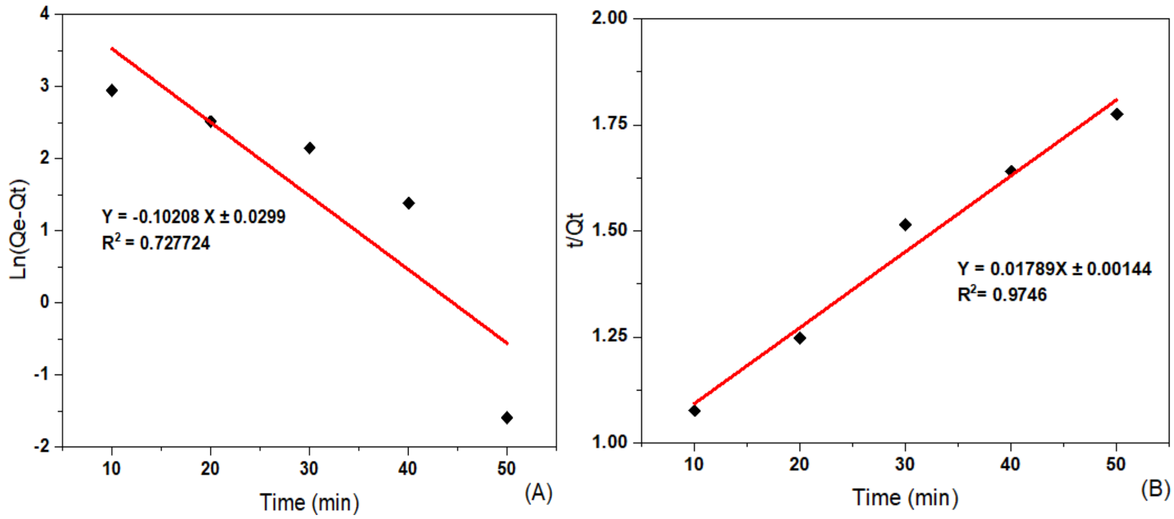

Figure 9. Kinetic of adsorption of hymexazol pesticide: (A) pseudo-first-order and (B) pseudo-second-order

According to the correlation factor, the adsorption results fit with pseudo second order ($R^2 >$ 0.9746) more than pseudo first order ($R^2 >$ 0.7277). This also means that the adsorption process was enhanced by chemisorption, which includes the sharing or exchange of electrons between the adsorbate and the adsorbent (Wekoye, 2020).

Adsorption isotherms

To understand the interaction between the CdO NPs and hemexazol pesticide, adsorption results should be fitted using isothermal adsorption. In this study, the Langmuir and Freundlich models were taken into account. The equation below illustrates the linear behaviour of Freundlich adsorption (Al-Ghouti, 2020)

$$log(Qe) = log(kf) + \frac{1}{n} log\,(Ce) \qquad (9)$$

Adsorption intensity and the adsorption capacity are represented by n and Kf, respectively, and are known as Freundlich constants. The kf is acquired from the intercept, and the n is gotten from the slope calculated 1/n.

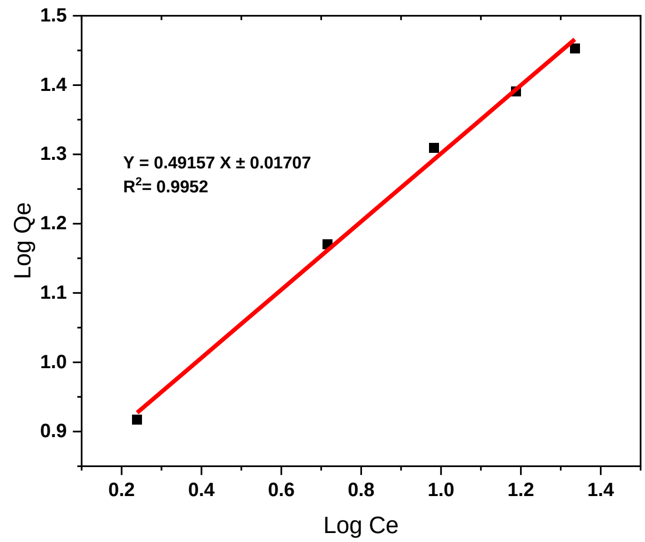

Figure 10. Freundlich isotherm for hymexazol pesticide adsorption at 298K

The value of 1/n of the Freundlich isotherm, which is 0.492, and these results are in agreement with favorable physical adsorption (Al-Ghouti, 2020).

The data are in accordance with the Langmuir adsorption, as given in the equation below (Patel, 2022).

$$\frac{Ce}{qe} = \frac{1}{(qmax)\ Kl} + \frac{Ce}{qmax} \qquad (10)$$

The maximum quantity of pesticide is q max (mg/g), while the Langmuir constant is KL (mg/L).

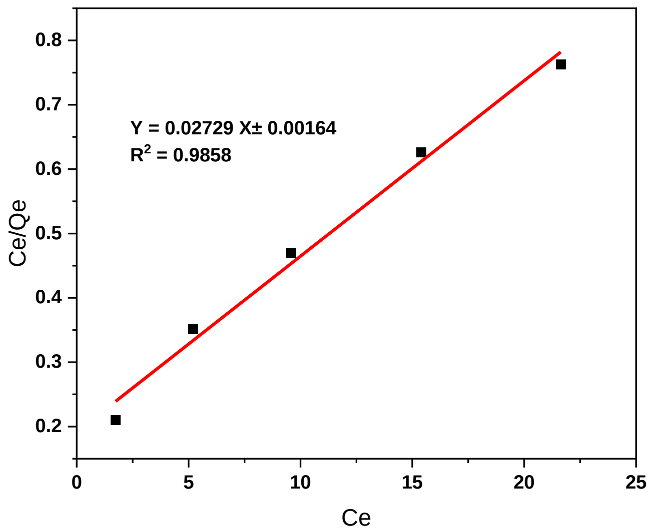

Figure 11. Langmuir isotherm for hymexazol pesticide adsorption on CdO NPs at 298 K

According to the values of the correlation coefficient (R^2), the Freundlich and Langmuir isotherm models both suit the adsorption results extremely closely. The efficiency of adsorption was measured by separation factor (RL) (How, 2022):

$$RL = \frac{1}{1+KL\ Ci} \qquad (11)$$

The RL value was found to be 0.0071, indicating that the hymexazol pesticide on the synthesized graphene oxide is favourable (Ashmawy, 2023).

Conclusion

This study focused on removing hymexazol pesticide from contaminated water using cadmium oxide nanoparticles synthesized by the photolysis method. The Synthesized CdO NPs was characterization using XRD, TEM, and FESEM. The adsorption results showed that CdO NPs is an excellent adsorbent material for adsorption of hymexazol pesticide, and this is due to the large surface area. The Equilibrium results were well fitted by the Freundlich isotherm model. The thermodynamic parameters ΔS°, ΔH°, and ΔG° were determined to be 52.24 (J/mol K), 14.97 (kJ/mol), and -0.779 (kJ/mol), respectively. Thus, it can be concluded that the adsorption of pesticide is endothermic and spontaneous process.

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